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# PRINCIPLES OF CHEMICAL GEOLOGY

A REVIEW OF THE APPLICATION OF THE EQUILIBRIUM THEORY TO GEOLOGICAL PROBLEMS

BY

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LONDON

WHITTAKER & CO.

2, WHITE HART STREET, PATERNOSTER SQUARE, E.C.

NEW YORK: 64 & 66, FIFTH AVENUE

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# PREFACE

The rapid progress of physical chemistry in recent years, especially in the conception of the conditions of equilibrium in solutions, has not failed to attract the attention of workers in the field of chemical geology. The importance of this branch of research is being almost daily emphasized by new developments, which promise to throw a much-needed light upon certain problems with which the geologist is confronted. At the same time, in this country, geologists have been slow to take up this line of research, possibly because a great deal of the work that has been done has been buried in the pages of foreign literature.

In the following pages I have endeavoured to indicate, as briefly as the subject permits, the main points of contact between recent chemical and physical researches and the various problems of geological chemistry.

To this end I have brought together a number of geological facts and problems which seem to fall under certain recognized principles of physical chemistry.

One of the main objects which I have endeavoured to keep in view has been to show that in all these

problems the key to the solution lies in the determination of the conditions of equilibrium.

The subject is so large that I have been compelled to be content in many cases with a bare allusion to work of the highest importance. I have also sacrificed to brevity a good deal of explanatory detail, the object being rather to stimulate interest in this branch of geology than to provide a complete exposition of the subject.

# CONTENTS


CHAPTER PAGE

I. Equilibrium between the Crystalline and Amorphous States - - - - - - 1

The States of Matter—Fusion Point of Minerals—The Fusion Curve.

II. Equilibrium as Influenced by Viscosity - - 19

General Considerations—Determination of Viscosity—Influence of Viscosity on the Fusion Curve—Superfusion Phenomena—Inoculation—Viscosity of Magmas—Influence on Rock Structure—Porphyritic Crystals—Influence of Varying Viscosity—Glassy Structures—Viscosity and Diffusion.

III. Diffusion as a Factor of Equilibrium - - 39

Diffusion of Gases—Diffusion of Solids—Diffusion of Liquids—Diffusion in Rock Magmas—Influence of Gravity—Phenomena of Assimilation.

IV. Surface Tension as a Factor of Equilibrium - 56

General Principles—Practical Application—Surface Tension and Crystal Growth—Supersolubility Curve—Influence of Co-solutes—Colloidal Suspension—Influence of Surface Tension on Chemical Action—Capillarity Phenomena—Adsorption Phenomena.

V. Vapour Pressure as a Factor of Equilibrium - 74

Dissociation Phenomena—Hydrated Minerals—Dissociation of Hydrates—Gypsum and Anhydrite—Hydrated Iron Oxides—Zeolites—Hydrolysis—Influence of Pressure on the Dissociation of Hydrates—Hydration and Dehydration in Nature.

CHAPTER PAGE

VI. Equilibrium Conditions of Polymorphous Forms - 98

Polymerism — Monotropic and Enantiotropic Substances—Sulphur—Wollastonite and Pseudo-Wollastonite—Quartz and Tridymite—Aluminium Silicates—Calcite and Aragonite—Other Polymorphous Forms—Magnesia Pyroxenes.

VII. Equilibrium in Solutions - - - - - 116

Solubility Curves in Aqueous Solutions—Application of Space Models to Igneous Magmas—Equilibrium of Two Liquid Phases — Application to Magmatic Differentiation.

VIII. The Eutectic Theory - - - - - - 136

Fusion Curve of Binary Systems — Application to Aqueous Solutions—Application to Alloys—Application to Fused Salts — Methods of Determining the Eutectic Composition — Comparison between Fused Salts and Solutions—Reversal of the Normal Order of Crystallization—The Eutectic Structure—The Ternary Eutectic Point.

IX. The Theory of Solid Solutions in Geology - 158

The Thermo-Dynamic Potential—Mix-Crystal Series, Type I.—Mix-Crystal Series, Type II.—Mix-Crystal Series, Type III.—Mix-Crystal Series, Type IV.—Mix-Crystal Series, Type V.—Conditions for the Formation of Mix-Crystals—Morphotropy—Mix-Crystals in Ternary Systems — Broken and Recurrent Series — Equilibrium Adjustments in Crystals on Cooling.

X. Chemical Equilibrium in Geology - - - - 184

General Principles — Reversible Reactions — Mass Action—The Solubility Product—Ionization of Fused Silicates—Influence of the Common Ion—Influence of Complex Ions—Velocity of Reaction—Catalysis—Influence of Pressure on Chemical Action—Influence of Strain.

Index to Authors - - - - - - 216

Index to Subjects - - - - - - 220

# PRINCIPLES OF CHEMICAL GEOLOGY

## I

### EQUILIBRIUM BETWEEN THE CRYSTALLINE AND AMORPHOUS STATES

The main object of the following pages is to present, in a concise form, the application of the principle of equilibrium to certain geological phenomena. To the student of geology nothing is at first sight more bewildering than the multiplicity of changes which rocks and minerals undergo in Nature. It is to chemical and physical laws that we are accustomed to look for an explanation of these transformations; but until comparatively recently many of these explanations were vague and hypothetical, owing to our ignorance of these laws.

The views of early writers, however, were greatly illuminated when, in 1884, Le Chatelier[1] announced the fundamental principle which regulates the direction in which any transformation tends to proceed. This principle states that any external change in the factors of equilibrium of a system is followed by a reverse change within the system. Thus, matter always tends to change in such a manner that the effect of changes in external conditions is opposed.

[1] *Le Chatelier*, Comptes Rendus, xcix. 786, 1884.

If the pressure on a system is increased, a new system, occupying a smaller volume, may be expected to be established; and if the temperature is raised, any new system will be that which is accompanied by an absorption of heat. The converse of this proposition is also true. If we know, therefore, the volume relations and heat effects of different transformations, the direction in which a change will proceed can generally be predicted. Van 't Hoff deduced the same law from thermo-dynamical principles, and expressed this law in mathematical terms.[1]

Simple, however, as this law may appear to be, there are almost insuperable difficulties in its application to geological problems, because we often know very little of the external and internal factors by which a state of equilibrium is determined. These difficulties will be gradually unfolded as the subject is further developed.

The States of Matter.—It will be convenient at the outset to replace the threefold division of matter into solids, liquids, and gases, by a more simple classification into *crystalline* and *amorphous* substances. The older distinction holds only with certain limitations, and, from the point of view of the equilibrium theory, breaks down under certain conditions; for many amorphous solids, as, for example, glassy substances, are more conveniently regarded as liquids of high viscosity, since they possess neither latent heat of fusion nor any definite melting point. Similarly the distinction between the liquid and gaseous phase disappears in the neighbourhood of the critical point.

The distinction between the amorphous and crystalline states is, on the other hand, clearly defined. The crystalline state is distinguished by vectorial properties, the amorphous state by scalar properties. Since, also, no substance can at once possess both vectorial

[1] *Van 't Hoff* and *Cohen*, Studien zur Chemischen Dynamik, p. 223.

and scalar properties, we can infer that the passage from the crystalline to the amorphous state is discontinuous, and is not marked by the presence of an intermediate stage, such as characterizes the passage from a liquid to a gas at its critical point.

This fundamental conception is of the utmost importance in the study of problems in geological physics. It affords a ready means of distinction between the two classes of matter. The distinction, also, involves other differences. Thus, for example, quartz crystal and quartz glass differ in their volume relations, and hence in their specific gravity. They differ, also, in their internal energy. At a certain temperature one or the other form becomes unstable, and tends to change into the more stable state. Under ordinary conditions, also, when the crystalline passes into the amorphous form, heat is absorbed, and when the converse change takes place heat is liberated.

It is convenient, therefore, to abandon the view that a liquid condition necessarily marks a definite state of matter as distinguished from the solid state. The discovery of so-called liquid crystals[1] shows that certain liquids may possess true vectorial properties, and resemble crystalline solids of weak cohesion. If slightly deformed, they return to their original shape, which is, in fact, the resultant of the force of surface tension, and the force by which molecular orientation is controlled.

We cannot, therefore, define the melting point, or fusion point, as the temperature at which liquefaction takes place, because in the case of many silicate minerals liquefaction is a gradual process, depending upon the rate of diminution of viscosity with rise in temperature. The true fusion point is the temperature

[1] *O. Lehmann*, Ann. d. Phys. (4), ii. 696, 1900; also Zeit. f. Kryst., xviii. 457-463, 1890.

of transition from the crystalline to the amorphous state. It will subsequently be shown that this point may be separated by many degrees from the point of apparent liquefaction.

Fusion Point of Minerals at Atmospheric Pressure.—There is, perhaps, no single experiment which, in the hands of different workers, has given such variable results as the determination of melting points. To some extent this has been due to the want of accurate methods of measuring high temperatures, but this is not the only reason. Even since the introduction of the Le Chatelier pyrometer, and other delicate methods of registering temperature changes, concordant results have not been obtained, and there is still a want of precise knowledge of the fusion points of many mineral substances.

Several methods of determining fusion points have been employed. These may be classified under the following heads: (1) Electrical, (2) volumetric, (3) optical, (4) thermal.

The electrical method depends upon the measurement of the variation in conductivity when a crystalline substance passes into a state of fusion. The volumetric method is based upon the observation of change of volume under the same circumstances. Each of these methods presents considerable difficulty in practice, and they have not been much used on that account.

The optical method has been applied in various ways, such as the examination by means of a telescope of splinters or powdered particles of the mineral substance when heated in the electrical furnace, the temperature being recorded by a pyrometer.[1] Doelter has increased the delicacy of this method by the use of the high temperature crystallization microscope, which has the advantage of enabling the whole process to be

[1] Tschermak. Min. u. Pet. Mitt., xx., 1901; xxi., 1902; xxii., 1903.

watched, and even photographed stage by stage.[1] Joly,[2] and also Cusack,[3] used an adaptation of the same method in their meldometer experiments, while Brun attempted to determine fusion points by comparison with Seger cones of known fusibility.[4] In all these variations of the optical method the exact temperature of the melting point is made to depend largely upon individual judgment. The personal equation, therefore, to some extent explains the variability of the results. Similar sources of error, combined with others of a more complex character, are involved in Åkerman's well-known calorimeter results.[5] The thermal method may be employed in various ways, of which the one most generally adopted is to find the point, either on the fusion curve or on the cooling curve, where a marked latent heat effect, due to change of state, is visible. This latent heat effect is the expression of the work done in breaking down, or building up, as the case may be, the crystalline structure. This is a method which has been largely followed in the case of metals and alloys. The difficulty, in the case of many silicates, lies in the fact that, owing to more or less internal friction, these substances often change their state from the crystalline state to the amorphous form so slowly that no abrupt change in the direction either of the heating or cooling curve can be detected. Even when chemically pure, many silicates do not possess a sharp melting point. The latent heat effect is distributed over so large an interval that it is impossible to state with precision at what temperature the change takes place. Nevertheless, this method has been followed with considerable success in some cases by

[1] Sitz. d. K. Akad. d. Wiss., cxv. 622, 1906.
[2] Proc. Roy. Irish Acad., Ser. 3, ii., 1891.
[3] *Ibid.*, Ser. 3, lv., 1896.
[4] Ann. de Sci. Phys. et Nat. de Genève, Ser. 4, xiii., 1902.
[5] Jernkontorets Annaler, 1886; also Stahl und Eisen, 1886.

Vogt,[1] as well as by Day and Allen[2] and other workers. In the practical application of the thermal method there is often a difference in the result depending upon whether the heating curve or the cooling curve is selected for the experiment. If, for example, a fused silicate refuses to crystallize on cooling, it is clear that the cooling curve can give no result.

This will be seen at once by the following consideration:

The simplest form of the time-temperature cooling curve of a pure crystalline substance of definite chemical composition is shown in the accompanying diagram (Fig. 1). AB shows the uniform fall in temperature

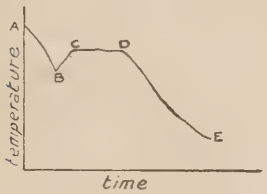


FIG. 1.—COOLING CURVE, SHOWING THE PASSAGE FROM AN AMORPHOUS TO A CRYSTALLINE STATE.

FIG. 2.—COOLING CURVE WITHOUT CHANGE OF STATE.

of the liquid phase on being cooled from A to the limit of superfusion at B, when crystallization sets in and the temperature rises suddenly to C, owing to the evolution of latent heat. This temperature, which is the true melting point, is maintained until the liquid phase has disappeared, when the temperature again falls uniformly along DE. If, on the other hand, the substance solidifies to a glass, as, for example, in the case of quartz or orthoclase, the cooling curve falls uniformly throughout its whole course, with no indication of the temperature at which solidification sets in (Fig. 2). Viscosity, in this case, prevents the molec-

[1] *Vogt*, Silikatschmelzlösungen, ii. 6 *et seq.*, 1904.
[2] Amer. Journ. Sci., xix. 93, 1905.

ular arrangement which characterizes the crystalline state.

Again, if crystallization only proceeds slowly, as is often the case in liquids of high viscosity, the evolution of heat may proceed at so slow a rate that the temperature fails to reach C (Fig. 1). The temperature to which a superfused liquid rises on crystallization, therefore, is not necessarily constant. For this reason the heat change on a cooling curve is, in the case of many silicates, less trustworthy than the heat change on a heating curve.

Viscosity, therefore, may introduce a serious difficulty in the determination of the melting points of silicate minerals by retarding the establishment of equilibrium conditions. It is only when the time-temperature curve shows a marked horizontality during the latent heat change that any definite result can be obtained in this manner. In spite of these difficulties, Day and Allen were able to detect an indication of heat absorption on the fusion curve of anorthite. They also found that the heating curve of anorthite glass shows a strong evolution of heat at 700° C., a temperature far below its melting point. This was evidently the point at which the viscosity of the glass was so far reduced that devitrification commenced, and the evolution of heat was the expression of the work done in crystallization.

So far we have only considered the fusion points of simple silicates in a pure state. In the case of mixed silicates, and of the class of substances included under the head of mix-crystals, other difficulties are involved. The same may be said of certain polymorphic substances, which undergo a transition into other forms at temperatures below their melting point. Thus, quartz generally changes into tridymite, and wollastonite into pseudo-wollastonite before the melting

point is reached. It is doubtful, therefore, whether the melting point of either quartz or wollastonite has ever been realized.

We come now to another definition of the melting point of a mineral based upon phase-rule terminology. The melting point of a mineral is that temperature at which the crystalline and amorphous phases are in equilibrium, or, in other words, the temperature at which both the crystalline solid and its molten product can coexist. In this case we have a single component system of two phases.[1] This system is, in the language of the phase rule, univariant. That is to say, on a temperature-pressure diagram the condition of equilibrium is represented by a curve, which is called the fusion curve.

The Fusion Curve.—No geological problem possesses greater interest or has given rise to more speculation than the influence of pressure upon the fusion point of crystalline solids, involving, as it does, the condition of the earth's interior and the phenomena of crystallization in the deep-seated portions of the lithosphere.

The problem may be studied on thermo-dynamical principles by the well-known formula:

$$\frac{dT}{dP} = \frac{1}{E} \cdot \frac{T}{L} (v' - v),$$

where P = the pressure;
L = the latent heat of fusion under pressure P;
T = the absolute temperature of fusion;
E = the mechanical equivalent of heat;
$v$ = the specific volume of the crystalline phase;
$v'$ = the specific volume of the amorphous phase.

It is evident that whatever may be the magnitude of the terms in the above equation, all the terms are

[1] The vapour phase is for the present left out of consideration.

positive except $(v'-v)$, which may be positive or negative according as fusion is accompanied by an increase or decrease in volume.[1]

Therefore the ratio $\frac{dT}{dP}$ must have the sign of $(v'-v)$.

If this is positive, the fusion point is raised by pressure; if it is negative, the fusion point is lowered by pressure. This general result follows also from the principle of Le Chatelier, which states that increase of pressure tends to produce that phase which has the smaller volume. In the ice type of fusion the crystalline phase has the larger volume, and increase of pressure accordingly lowers the fusion point. This type of fusion is found to exist under normal atmospheric pressure not only in the case of ice, but also in the case of bismuth, arsenious oxide, and many borates. This circumstance has led some geologists to surmise that silicates might also follow this rule—a conclusion, however, which has been disproved by the experiments of Barus,[2] Roberts-Austen and Rücker,[3] Doelter[4] and others. The fact is, therefore, established that crystalline silicates, within the limits of experiment, follow what may be called the normal type of fusion, and at moderate pressures expand on assuming the liquid state.

We are not now concerned with the actual amount of influence which pressure exerts upon the fusion point, as this obviously depends upon the change of volume and the value of the latent heat factor. It may be stated that the effect in general appears to be small, and in the case of ice it requires an increase of pressure of 135 atmospheres to lower the melting point 1° C.

[1] The question of a possible negative latent heat of fusion, as suggested by Tammann, is not here considered.

[2] Phil. Mag., xxxv. 173, 1893.

[3] *Ibid.*, xxxii. 353, 1891.

[4] Neues Jahrbuch f. Min. ii. 141, 1901.

Up to pressures of a few hundred atmospheres the fusion curve has been found to be a straight line.[1] At higher pressures the fusion curve has been found to be concave to the pressure axis,[2] and should, therefore, if followed far enough, exhibit a maximum point. This maximum, as calculated by Tammann, corresponds to a pressure of 40,000 atmospheres, and requires a depth in the earth's crust of about 150 kilometres.[3]

The problem now to be considered is what course the fusion curve takes at greater pressures than have hitherto been experimentally realized. Ostwald,[4] and likewise Poynting,[5] have suggested that the upper limit of the fusion curve may be a critical point. Ostwald bases this hypothesis upon several considerations. He maintains that the experiments of Tresca[6] and Spring[7] tend to show that many crystalline bodies become plastic under high pressures. He regards the so-called liquid crystals as solids which are near their critical point at ordinary pressures. He considers that the effect of pressure is to diminish vectorial properties, and tends to reduce all matter to an isotropic state.[8]

This view, however, presents serious difficulties, and has been opposed by Tammann,[9] Planck,[10] Roozeboom,[11] and others. Tammann's experiments point to the conclusion that, while the volume difference between the crystalline and amorphous states diminishes rapidly at high pressures, the value of the latent heat factor

[1] *Barus*, Amer. Journ. Sci., xlii. 125, 1892 ; *Mack*, Comptes Rendus, cxxvii. 361, 1898 ; *Hulett*, Zeit. f. Phys. Chem., xxxviii. 629, 1899.
[2] *Barus*, Amer. Journ. Sci., xlii. 125, 1892 ; Bull. U.S. Geol. Surv., No. 96, 1892 ; *Damien*, Comptes Rendus, cviii. 1160, 1889 ; *Demerliac*, *ibid.*, cxxiv. 75, 1897 ; *Tammann*, Ann. d. Phys., lxviii. 553, 629, 1899.
[3] See also *Doelter*, Zum Physik des Vulkanismus.
[4] Lehrbuch, ii. 2, 373. [5] *Poynting*, Phil. Mag., xii. 32, 1881.
[6] Mém. prés. à l'Institut, 1868, 1872.
[7] Zeit. f. Phys. Chem., xv. 391. [8] Allg. Chem., ii. 391.
[9] Kristallisieren und Schmelzen, Leipzig, 1903.
[10] Wied. Ann., xv. 446, 1882.
[11] Die Heterogenen Gleichgewichte, i. 91.

changes but little. Hence it is obvious that the values of $(v'-v)$ and of L in the above fundamental equation do not simultaneously pass through zero, and, therefore, the fusion curve cannot end in a critical point.

Although, therefore, we are without precise experimental knowledge of the ultimate effect of very high pressures upon the conditions of equilibrium between the crystalline and amorphous states, much can be reasonably inferred from a consideration of the general equation to the fusion curve. Thus, if this curve

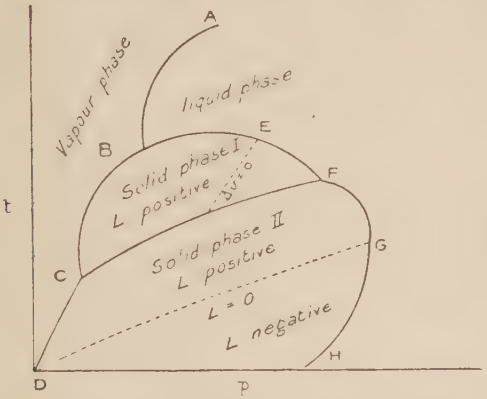


FIG. 3.—HYPOTHETICAL FUSION CURVE ON A TEMPERATURE-PRESSURE DIAGRAM. (AFTER TAMMANN.)

passes through a maximum point, at which the value of $(v'-v)$ is zero, the latter factor will be expected, from mathematical considerations, to undergo subsequently a reversal of sign. Reasoning in this way, Tammann has arrived at some interesting conclusions, which we will now proceed to examine.

Tammann's argument is made clearer by a consideration of the diagram (Fig. 3) in which—

AB is the vapour tension curve of the liquid phase.
BC „ „ „ „ solid phase I.
CD „ „ „ „ „ „ II.
BEF is the fusion curve of the solid phase I.
FGH „ „ „ „ „ „ II.
CF is the transition curve of the two polymorphic forms, I, II.

The points B, C, F are triple points in phase-rule terminology. At E, which is the maximum fusion point, the volume change is zero. To the left of this point $(v'-v)$ is positive and the fusion is normal ; to the right of E we have the ice type of fusion with $(v'-v)$ negative. At G the latent heat is zero, and below this point is the second fusion curve FGH, along which the latent heat is negative. The occurrence of polymorphic forms with a transition curve CF is, of course, purely hypothetical, but does nevertheless occur in certain silicates. Although, however, the above results follow mathematically from the consideration of the equation—

$$\frac{dT}{dP} = \frac{1}{E} \cdot \frac{T}{L} (v'-v),$$

the assumption that the latent heat value passes through zero and changes its sign does not rest upon any experimental basis. Tammann, however, advances reasons for the assumption that the crystalline state is only stable within the region bounded by a continuous curve. It is known that a fused salt may, under certain conditions, be cooled below the temperature at which crystallization should set in. In this superfused condition the tendency to spontaneous crystallization is at first very feeble, if not entirely absent. It then attains a maximum, after which, at a still lower temperature, it declines again. Tammann concludes that if the temperature is lowered sufficiently under constant pressure, a point is at length reached at which equilibrium between the crystalline and amorphous states is again established. In other words, there is a second fusion curve, having properties the reverse of those of the upper fusion curve. In this connection it is interesting to note that Tammann has found that water at sufficiently high pressures crystallizes in an ice modification which has a smaller specific volume

than water. Duhem, while accepting Tammann's facts with regard to the possibility of the existence of a lower fusion curve, attributes this to a curve of false equilibrium.[1] In support of this view it should be mentioned that Van 't Hoff has found so many cases of lagging and apparently false equilibria, that great care must be exercised in assuming that a condition of equilibrium exists, when in reality we may be dealing with a persistent labile phase marked by extreme slowness of transition.[2] On the other hand, Raoult Pictet believed that he had detected an actual example of a double fusion curve in the case of chloroform,[3] and O. Lehmann describes a similar example in the case of selenium,[4] neither of which observations, however, has yet been confirmed.

To the geologist the hypothesis of a second fusion curve at low temperatures and high pressures seems to possess but little practical importance, but Tammann's theory of a maximum fusion point at which the volume change alters its sign has an interesting bearing upon the nature of the earth's interior, to which reference will be made hereafter.

Distinction between Uniform Pressure and Stress.—In any attempt to explain the conditions of equilibrium between the crystalline and amorphous forms of matter, as illustrating geological phenomena, it is necessary to distinguish between uniform statical pressure and shearing stress. The former acts equally in all directions, while the latter acts in certain directions only. Ostwald illustrates the latter by the analogy of the winepress in which, while the solid portion of the fruit is subjected to a certain pressure in one direction, the escaping liquid is free to move in

[1] Archives Néerlandaises, Ser. 2, vi. 93, 1901.
[2] *Ibid.*, Ser. 2, vi. 487, 1901.
[3] Zeit. f. Phys. Chem., xvi. 422-425, 1895.
[4] Molekularphysik, i. 712.

another direction.[1] The equilibrium conditions in such cases differ entirely from those which result from uniform static pressure. In Nature a familiar example is afforded by glacial ice, acted upon by stresses in certain directions. The action in this case closely resembles the winepress. Portions of the ice are melted by stress, the water so formed being squeezed out, and freezing again where the pressure is not experienced. The solid and liquid phases in this case do not experience the same increase of pressure. This may be considered mathematically thus:

If a solid and a liquid phase are in equilibrium, and the pressure on the solid phase is increased by an amount $P_1$, equilibrium is only restored by increasing the pressure on the liquid phase by an amount $P_2$, the increase of pressures being inversely proportional to the specific volumes of the two phases, thus:

$$\frac{dP_1}{dP_2} = \frac{V_2}{V_1}.$$

The result is more clearly shown by the graphic illustration given by Roozeboom,[2] Fig. 4.

If $L_1$ and $S_1$ are the vapour pressure curves of liquid and solid phases at any pressure, and $L_2$ and $S_2$ are the corresponding curves at any higher pressure, then the intersections of these curves will be the melting points of the solid phase under particular conditions. Thus under the original pressure, acting on both phases, the melting point is at A. Under higher pressure, acting on both phases, the melting point is raised to B. If the solid phase alone experiences the increased pressure, the melting point will be at C, the intersection of $L_1$ and $S_2$. The latter result is the same whether the solid expands or contracts on liquefying.

[1] Allg. Chem., ii. 378.
[2] Die Heterogenen Gleichgewichte, i. 214, 215.

Thus, the effect of a stress acting upon the solid phase only is to lower its melting point.

Similar results follow from the action of tensile forces or strains.[1] Unfortunately, the only quantitative results hitherto obtained refer to ice, and we are without definite knowledge of the amount by which the melting points of minerals are lowered by this means. The general result, however, is important, since it shows that all solids, whether they expand or contract on melting, under certain circumstances

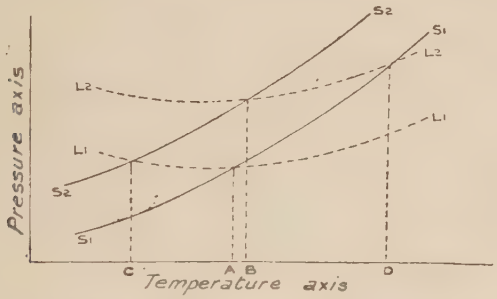


FIG. 4.—DIAGRAM ILLUSTRATING THE INFLUENCE OF STRESS UPON THE FUSION POINT. (AFTER ROOZEBOOM.)

have their melting points lowered by strains or stresses.[2]

The phenomena of ice-flow may, however, resemble in some respects the formation of schists in heated regions of the earth's crust, where the rocks are already near the melting point; but it is difficult to separate the purely mechanical action resulting from strains and stresses from the effects of increased solubility and chemical action accompanying them.

In this connection we may consider the influence of mechanical flow upon the equilibrium of the crystal-

[1] *Riecke*, Ann. d. Phys. N. F., liv. 731, 1895.
[2] *Ostwald*, Allg. Chem., ii. 378.

line and amorphous states. Quite recently additional light appears to have been thrown upon this point by the researches of Beilby on the behaviour of metals and crystalline minerals under the influence of mechanical flow. He has advanced experimental reasons for concluding that the strain slip set up by the deformation of crystalline grains is arrested at a certain stage by the development of films of hard, non-plastic, amorphous substance along the surfaces where movement takes place. The result is that the remains of the crystalline grains become embedded in a vitreous matrix, which prevents the further yielding of the mass by flow. By the application of heat the crystalline structure is fully restored. He is thus led to the conclusion that all crystalline bodies possess the property of passing from the crystalline to the amorphous state by mechanical flow, and from the amorphous to the crystalline state by heat, at a definite transition temperature below the fusion point. Beilby has extended his observations on surface flow and the passage from the crystalline to the amorphous state not only to those metals which can be readily obtained in a pure state, such as silver, gold, platinum, copper, lead, antimony, and bismuth, but also to certain minerals, such as Iceland spar and quartz. He is inclined to the conclusion that between the crystalline and the hard amorphous phase there is an intermediate mobile phase. He maintains that the smooth surface upon polished minerals is due to a flowed layer, which forms a kind of varnish of amorphous matter. When crystalline powders are welded into cakes by pressure, it is, in his opinion, the amorphous phase, resulting from flow, which supplies the cementing material. The transition point, at which the amorphous phase becomes crystalline, in the case of silver, was found to be about 700° C. below the

melting point of this metal; and he concludes that at a sufficiently low temperature the amorphous phase is stable, and would be the permanent form assumed by all matter at that temperature if crystallization could in the meantime be prevented. The physical explanation of this stability of the amorphous phase may be, he thinks, explained as follows: The crystalline state may be regarded as the outward manifestation of a dynamic equilibrium between a primary cohesive force and the repulsive force of molecular vibration, or, what is the same thing, the kinetic energy imparted by heat. This assumption he believes to be supported by the great increase in the tensile strength of metals at the low temperature of liquid air, at which temperature the primary cohesive force is opposed by only a very feeble repulsive force, due to molecular vibration.[1]

In the classical experiments of Adams and Nicolson on the flow of marble,[2] there is nothing to indicate that the deformed calcite crystals ever assumed an amorphous condition; nor has such a transition been noted in any of the investigations of Daubrée and others, although high pressures, reaching in some cases to 25,000 atmospheres, were employed. In all these cases, however, the heat effect must have been considerable, and the rocks upon which the experiments were performed were probably raised above the transition temperature. There is, in fact, nothing to preclude the possibility of a temporary intermediate amorphous phase, which was almost immediately transformed into the crystalline state after the molecular adjustments had been completed. This view

[1] Proc. Roy. Soc., lxxii. 218, 1903; also Section B, British Association, South Africa meeting, 1905. Ewing, in his presidential address before Section G at York, 1906, accepts these views.

[2] Phil. Trans., cxcv. 363.

has been expressed by Lehmann, who explains the phenomenon occasionally observed in gneiss — of quartz crystals bent round undeformed felspar crystals, as the result of the formation of an intermediate amorphous form during the deformation of the original rock.

## II

### EQUILIBRIUM AS INFLUENCED BY VISCOSITY

As we have seen, viscosity plays an important part in retarding the transition of minerals. It is necessary, therefore, to examine this property more closely. Viscosity may be defined as that property of a substance owing to which resistance is offered to the relative motion of its parts. In the case of most true solids its value is infinite.[1] In liquids it may be regarded as the net result of two distinct forces—viz., a frictional force during the contact of molecules, and an attractive force which exerts a resistance to forces tending to move one molecule past another.[2] It is not easy to express viscosity quantitatively, but if $\eta$ represent the coefficient of viscosity of a liquid, and if a stratum of thickness $c$ has a velocity V at the surface and a velocity of zero at the base, then the tangential stress acting across each unit of surface is proportional to the velocity gradient $\frac{V}{c}$, and is equal to $\eta \frac{V}{c}$. Thus, viscosity may be defined as the ratio of the tangential stress to the velocity gradient.[3] There is a close analogy between viscous stress in a liquid and the shearing stress in a strained solid. Viscous stress is related to velocity as shearing stress is to the displacement.

[1] *Maxwell*, Scientific Papers, ii. 620.

[2] *Thorpe* and *Rodger*, Phil. Trans., Bakerian Lecture, clxxxv. 308, 1894.

[3] *Newton*, Principia, lib. ii., sec. 9.

The coefficient of viscosity of liquids usually d minishes very rapidly as the temperature increase Thorpe and Rodger[1] have shown that the viscosit of water at 80° C. is only about one-third of its valu at 10° C. The influence of pressure on viscosity ha been investigated by Cohen.[2] It appears to vary wit the nature of the fluid. The effect of pressure i largely annulled by even a small increase of tem perature. Thus, in the case of pure water at a tem perature of 1° C. the influence of a compression o 600 atmospheres, calculated as percentage increas of viscosity, was found to be more than six time as large as at 23° C. A saturated solution of commo salt behaved otherwise, the viscosity increasin with pressure nearly in direct proportion, and i this case the influence of temperature was les marked. If, therefore, magmas behave as saturate salt solutions, Cohen's investigations would indicat an increase of viscosity in direct proportion to th pressure. For this reason Doelter has ascribed t increased viscosity the rarity of fine apophyses i deep-seated intrusions.[3] It is possible, however, tha this may be due to the absence of open fissures a depths where pressure is great. The experiment of Oetling[4] and Amagat[5] led them to conclude tha high pressures promote fluidity, but the results ar not conclusive. A high state of fluidity in som magmas is proved by the extreme length of thi apophyses, and their frequent penetration into minut cracks of the invaded rock.[6] This fluidity, howeve is probably due to causes other than pressur

[1] *Op. cit.* [2] Ann. d. Phys. u. Chem., xlv. 666, 189
[3] Physikalisch-Chemische Mineralogie, p. 110.
[4] Tschermak. Min. u. Pet. Mitt., xvii. 331, 1897-98.
[5] Comptes Rendus, No. 16, 1893.
[6] *Iddings*, Journ. Geol., i. 833, 1893; *Geikie*, Ancient Volcanoes o the British Isles, ii. 413, 422, 439, 1897.

such as the temperature and composition of the magma.

Determination of Viscosity.—The measurement of internal molecular friction has been attempted by Fousserau by determining the time, T, taken by the fluid to flow through a capillary tube under the influence of a pressure, P. The time, T′, taken by water to flow under the same conditions is also measured, and the density of the fluid, $\delta$, is found. Then, if $\eta_1$ is the coefficient of viscosity of water, and $\eta$ that of the fluid, $\frac{\eta}{\eta_1} = \frac{T}{T'}\delta$. Fousserau adapted this method to certain fused salts,[1] but it presents great difficulties in practice. In the case of fused salts T varies enormously with changes of temperature, and is generally very great in comparison with T′, while the density cannot be easily determined. Helmholtz and Pietrowski attempted to arrive at the same result by observing the oscillations of a sphere filled with the given fluid, and König adopted the method of causing a sphere to swing immersed in the fluid Jones used a modification of this method by observation of a sphere allowed to fall freely through the liquid.[2] All these methods are difficult to apply in the case of fused silicates, on account of the small practicable volume and the high viscosity of the fused substance. For purposes of comparison in the case of individual silicates, Doelter recommends the measurement of the penetration of a platinum needle weighing 165 grammes ; but the method is wanting in delicacy, for with very viscous substances the platinum only sinks in about $\frac{1}{2}$ millimetre, and with slightly viscous minerals it sinks to the bottom.[3] As an example of the great range in viscosity exhibited by different substances, it may be stated that glycerin

[1] Ann. de Chim. et de Phys., vi., t. v., 360, 1885.
[2] Phil. Mag., xxxvii. 451, 1894.
[3] *Op. cit.*, p. 636.

shows a viscosity forty-two times as great as that of water, and fused silicates are often very much more viscous than glycerin. In fact, compared with water, $\eta$ is so much greater than $\eta_1$ that the ratio $\frac{\eta}{\eta_1}$ for different silicates becomes almost valueless for comparative purposes. As the result of rough measurement, it appears that whereas the viscosity of augite, hornblende, magnetite, and fayalite suddenly diminishes at their fusion point, that of quartz, leucite, nepheline, albite, and orthoclase only diminishes very gradually, and the latter minerals lose their crystalline structure long before they become really fluid. Similarly, the same minerals do not at once separate in a crystalline form when cooled below their fusion points, their velocity of crystallization being retarded by viscosity, giving rise to marked superfusion.[1]

Influence of Viscosity on the Fusion Curve.—The influence of viscosity upon the fusion curve of certain silicates has recently been investigated by Day and Allen.[2] A metal, such as gold or silver, shows a sudden, sharp bend in the fusion curve at a definite temperature, which is the melting point. A silicate mineral of low viscosity, such as anorthite, presents a similar flexure, although it is less sudden. In felspars of the anorthite-albite series the flexures become less pronounced as the viscosity of the mineral increases. The viscosity increases with the proportion of the albite molecule, with the result that it gradually becomes more and more difficult to determine from the fusion-curve at what temperature melting begins to take place.

[1] *Doelter, op. cit.*, pp. 639-643.

[2] Amer. Journ. Sci., xix. 93, 1905. The results obtained by Day and Allen have been criticized by Doelter on the ground that the artificial felspars prepared by them were not necessarily identical with the natural minerals.

Ultra-viscous bodies appear to melt over a considerable range of temperature, and have no sharp melting point. All trace of the latent heat of fusion is lost in the case of glasses, the difference between the liquid and solid state being due to viscosity only, and not to change of state.

Another point noticed by Day and Allen was the persistence of the crystalline state in albite at a temperature at which it should have been liquid, showing that viscosity was still too great to permit the deorientation of the molecules to take place. This phenomenon had been previously described by Mallard as "crystalline surfusion."

Superfusion Phenomena.—In the case of supersaturated aqueous solutions, as will be seen later, surface tension is one of the chief controlling factors, and viscosity plays a subordinate part. In the superfusion phenomena of silicate magmas, however, internal molecular friction assumes an important rôle in the equilibrium conditions.

Doelter states that the more complex silicates, when fused, usually decompose and form simpler combinations. Viscosity in this case may impede crystallization to such a degree that the simple forms separate on cooling instead of the original compound. Thus, garnet[1] after fusion crystallizes as a mixture of lime olivine ($Ca_2SiO_4$) and anorthite ($CaO.Al_2O_3.2SiO_2$). Many other apparently anomalous phenomena in fused silicates may possibly be explained in a similar way by the small rate of molecular reaction owing to viscosity.[2]

The view that viscosity has an influence upon the facility with which molecules can combine on solidification has also been advanced by Barus and Iddings.

[1] *Vogt*, Silikatschmelzlösungen, i. 93.
[2] *Doelter*, Zeit. f. Electrochem., xii. 413, 414, 1906.

Experiments on the electric conductivity of fused silicates seem to show that those substances which possess the lowest electric conductivity, and are, therefore, but little dissociated, are also those which most readily crystallize from fusion. They found, also, that the conductivity of magmas increases with rise of temperature, which implies less "ionic viscosity." Pure silica, however, possesses a low conductivity, and seems to be an exception to this view. It is noteworthy, in this connection, that quartz and magnetite often crystallize independently in igneous magmas, instead of combining to form an iron silicate.

Superfusion in magmas, therefore, although it is analogous to supersaturation in aqueous salt solutions, is a more complex phenomenon, owing to the greater influence of viscosity. The property of superfusion belongs in greater or less degree to all substances.

It is not possible, in the present state of our knowledge, to establish any quantitative relation between viscosity and superfusion; but it is evident that anything which tends to delay the establishment of equilibrium must influence the number of centres of crystallization formed in a given time. Since, also, viscosity increases as the temperature falls, the labile state must differ from the metastable state in possessing a higher degree of viscosity, when both freedom of molecular motion and the tendency to crystallize will be checked by internal friction. Thus viscosity is an important factor in retarding transformations and inducing conditions of false equilibrium. Transition points can, from this cause, be overstepped in either direction. It is important to note, however, that the laws of viscosity merely retard, and do not inhibit, molecular movement. The time factor becomes important.

In this connection, Tammann has shown that if the

velocity of crystallization is plotted against the degree of superfusion, the curve of crystallization velocity attains a maximum, and then rapidly declines.[1] The region A here corresponds to the metastable region of Ostwald, and is usually characterized by large and well-formed crystals (Fig. 5), while the region B to C corresponds to the labile region, where crystals are small and often imperfect. The rate of cooling determines the facility with which the labile state is reached, and thus influences the size of the crystals. Thus,

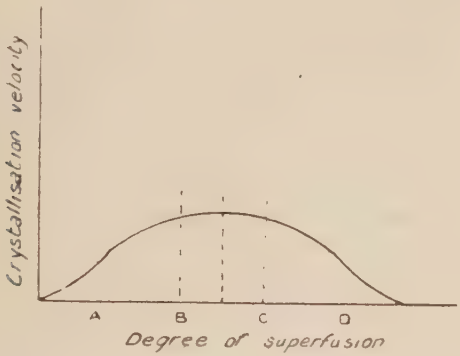


FIG. 5.—DIAGRAM ILLUSTRATING THE VARIATION IN THE VELOCITY OF CRYSTALLIZATION AT DIFFERENT DEGREES OF SUPERFUSION.

andesites are commonly characterized by two generations of felspar, of which the first are regarded by Miers as produced in the metastable region, and the second in the labile region. In the plutonic representatives of these rocks, however, owing to the conditions of crystallization, the labile state is seldom attained, and the two generations of felspar are rarely exhibited.

INOCULATION.—In the metastable region crystallization will not take place in the absence of crystalline

[1] Zeit. f. Phys. Chem., xxvi. 307, 1898.

nuclei. Seeing that not only crystals of various kinds, but also crystalline nuclei, may float up from below, or may travel along convection currents from one part of a magma to another, it is of great interest to note certain experiments which have been performed in inoculating fused silicates with solid crystals of various kinds. The results are not so satisfactory as in aqueous solutions of salts, because of the restriction of the area which is influenced by the inoculating body. Doelter states that fused hornblende, inoculated with olivine, consolidates as a mixture of augite and newly-formed olivine crystals.[1] Vukits found that a fused mixture containing 90 per cent. augite and 10 per cent. olivine, when inoculated with augite, consolidated as augite, whereas without inoculation olivine separates.[2] Vučnik found that a fused mixture of hedenbergite and anorthite, in the proportion of 3 : 1, gave, without inoculation, at first hedenbergite crystals; but on inoculating with anorthite, only a few hedenbergite crystals separated, the greater part being resolved into magnetite and glass;[3] while in some cases the order of separation was reversed, and anorthite was the first to separate. In another experiment, in a fused mixture of albite and olivine, in the proportion of 4 : 1, olivine crystals alone separated when the mixture was inoculated with olivine. These experiments show that inoculation with crystalline bodies may in certain cases influence the crystallization of magmas, and may even invert the normal order of separation of the minerals present. These results are most marked in the least viscous magmas. It may be possible that the small felspar laths which frequently occur in parallel arrangement around the larger felspars in certain porphyritic rocks may owe

[1] Physikalisch-Chemische Mineralogie, p. 103.
[2] Centr. f. Min., p. 716, 1904.
[3] *Doelter, op. cit.*, p. 104.

their separation to the inoculating influence of the larger crystals, whereby the superfusion of the surrounding magma was neutralized. Harker, however, concludes that inoculation has very little effect upon the crystallization of igneous rock magmas, owing to the relative scarcity of foreign bodies except near the margin. It seems to be certain that viscosity will generally greatly restrict the sphere of influence of the inoculating body.[1]

Viscosity of Magmas.—Vogt's researches on slags led him to the conclusion that the rate of diminution of viscosity with rise of temperature is greater for those of basic than for those of acid composition. The presence, also, of certain substances has a marked influence upon the viscosity of the slag. Thus, fluidity is promoted by the presence of FeO, MnO, and PbO; while a preponderance of $K_2O$ or $Al_2O_3$ causes a decided increase in viscosity, especially in acid slags. Slags rich in lime, also, are more viscous than those rich in magnesia; but basic slags of the composition of melilite and gehlenite, containing nearly equal quantities of CaO, MgO, and $Al_2O_3$ are very fluid, but not so fluid as the fayalite slags.[2]

Doelter has obtained the following sequence of viscosity for various rock magmas, which are arranged in the order of increasing viscosity:

1. Limburgite, augitite, plagioclase basalt, diabase.
2. Leucite lava, tephrite, leucitite, gabbro, basic monzonite.
3. Nephelinite, nepheline basalt, diorite, syenite, monzonite.
4. Nepheline-syenite, phonolite.
5. Granite, obsidian, rhyolite.

[1] Natural History of Igneous Rocks, p. 210, 1909.
[2] Silikatschmelzlösungen, ii. 161, 162, 1904.

The above, however, refers rather to molten rocks than to rock magmas, which generally contain volatile fluxes. In general the viscosity of molten rocks increases with their silica percentage. It is not known, however, to what extent the more viscous rocks would develop greater fluidity at temperatures considerably above their melting points. The phenomena of dry fusion, as illustrated by slags, probably differ materially from those of aqueo-igneous fusion, such as characterize the majority of rock magmas. Barus found that water at temperatures between 185° C. and 200° C. will so impregnate glass that this substance becomes fusible below 200° C. The solution is accompanied by contraction in volume, and would, therefore, be promoted by pressure. He concludes that glass is miscible with water in all proportions.[1] It is probable, therefore, that the presence of superheated water greatly diminishes the viscosity of silicate magmas, at the same time lowering their fusion point. Vogt thinks that this influence of water is greater in the case of basic magmas than with those of a more acid character. Harker, however, is inclined to agree with the view of Fouqué and Michel Lévy that volatile fluxes are more common in acid magmas, which, therefore, under like conditions, crystallize at lower temperatures than basic magmas. Whether the presence of these fluxes would counteract the greater natural viscosity of acid magmas is uncertain.

Influence of Viscosity on Rock Structure.—Rock structure is largely influenced by the facility with which certain minerals crystallize and by the velocity of their formation. The order of crystallization tendency for certain rock-forming minerals is as follows: (1) Corundum, iron-glance, spinel; (2) magnetite, olivine, hypersthene, augite; (3) nepheline, anorthite; (4) labra-

[1] Amer. Journ. Sci., vi. 270, 1878; *ibid.*, ix. 61-375, 1900.

dorite, leucite; (5) diopside; (6) albite, orthoclase, quartz.[1]

Crystallization velocity, or the rapidity of crystal growth, is also a variable factor. Thus magnetite with a high crystallization tendency has a low crystallization velocity, and tends to form many centres of crystallization, but small crystals. Nepheline has a smaller crystallization velocity than anorthite, hence skeleton crystals of the former often occur in slags.

The crystallization velocity is a vectorial property in all mineral species, some crystalline faces growing at a more rapid rate than others. We shall see that this feature is largely influenced by surface tension; but it is also dependent upon the degree of superfusion, and consequently by the viscosity of the medium. As the viscosity increases the crystals generally show a tendency to be elongated, acicular, or lath-shaped in form. Stout forms are more characteristic of growth in the earlier stages of consolidation, when viscosity is less pronounced. Mix-crystals show great differences both in crystallization tendency and velocity of growth. Thus, in olivine these characters both increase rapidly in proportion to the amount of iron present in their composition. That viscosity has an important influence upon the size of crystals is supported by the fact that in many alloys, and in some highly fluid slags, large individuals are commonly produced even by rapid cooling.

Growth of Porphyritic Crystals.—The increase of internal friction resulting from viscosity would lead

[1] *Doelter*, Physikalisch-Chemische Mineralogie, p. 112; also *Vogt*, Silikatschmelzlösungen. It is of interest to note that this order is approximately the same as the order of resistance of these minerals in a fused state to the electric current. Whether, however, the tendency to crystallize from fusion is related to the degree of dissociation of the molecules, as measured by conductivity, is not known. On this subject, see *Barus* and *Iddings*, Amer. Journ. Sci., xliv. 242, 1892.

to the conclusion that porphyritic crystals would not develop in a highly viscous magma. The end products of crystallization, therefore, should be either glassy or micro-crystalline. In many cases this is borne out by facts, but there are apparent exceptions, as, for example, the coarse-grained structure of some segregation veins. The acid residuum of magmas may consolidate either as fine-grained aplites or as giant pegmatites. This can be explained by the influence of magmatic water in diminishing viscosity, as suggested by Arrhenius[1] and others. This may also account for the difficulty experienced in obtaining crystals of albite by dry fusion, whereas these readily separate from natural magmas. The escape of magmatic water, therefore, promotes the viscosity of magmas, and thus influences the character of the resulting crystals. The growth of large crystals seems also to be influenced by somewhat obscure factors. Amongst these the nature of the substance is of great importance. Retgers thinks that each crystalline substance has its own fixed maximum growth,[2] beyond which it will remain unchanged even in contact with a supersaturated solution of its own mother liquor. It has also been established that the addition of certain substances facilitates the formation of large crystals. Thus, copper chloride favours the formation of large sodium chloride crystals in a solution of common salt. Many other substances also act as crystallizing agents, both in watery solutions and in slags.[3] These results may be due to surface tension phenomena, and the influence of diffusion as affecting concentration currents in the mother liquor, as indicated by the researches of Wulff,[4] may also be a controlling factor. In this way may possibly be

[1] Zur Phys. des Vulkanismus, Geol. Fören, bd. xxii.
[2] Zeit. f. Phys. Chem., ix. 278, 1892.
[3] *Doelter*, Physikalisch-Chemische Mineralogie, p. 191.
[4] *Ibid.*, p. 192.

explained the formation of two generations of the same mineral, the second generation of smaller crystals being formed under conditions of greater viscosity of the magma, and the observations of Miers[1] may, in this sense, be true.

In explaining the growth of porphyritic crystals the possibility also exists that these may sometimes be of intratelluric origin, as suggested, amongst others, by Rosenbusch. This mode of origin will not hold in all cases, however, as has been shown by Zirkel,[2] Pirrson,[3] and Harker;[4] while Vogt has shown that porphyritic crystals can form *in situ*, even by quick cooling, in magmas of a certain composition.

The porphyritic structure, therefore, may be regarded as a normal result of crystallization under certain conditions; and, although in the case of eruptive rocks large crystals may float up from below, it is by no means necessary to look upon them as always formed in this way.

It is interesting to note, as Harker remarks,[5] that porphyritic crystals evenly diffused show that there was sufficient viscosity to prevent them from sinking.

Influence of Varying Viscosity.—Durocher suggested that the late consolidation of quartz in many igneous rocks might be the result of a wide range of viscosity and a comparatively feeble tendency to assume the crystalline condition. Joly has extended this theory to explain not only the late crystallization of quartz, but also the normal order of separation of silicates from molten magmas.[6] He suggests that the viscosity phenomena of pure silica may be additive, the silicates possessing increased viscosity in proportion to

[1] See *ante*, p. 25.
[2] Lehrbuch, i. 737, 1893.
[3] Amer. Journ. Sci., vii., 1899.
[4] Tertiary Igneous Rocks of Skye, p. 270, 1905.
[5] Natural History of Igneous Rocks, p. 322.
[6] Proc. Roy. Dub. Soc., ix. 298-303, 1900-01.

their silica percentage. This view is strengthened by the results obtained by Day and Allen,[1] who found that viscosity and reluctance to crystallize were greater in proportion to the increase in the ratio of albite to anorthite in the lime-soda series of felspars. The many reversals of the normal order of crystallization, however, are not easy to reconcile with this view.[2]

The presence of other minerals, again, by lowering the viscosity, may promote the separation of crystals which would otherwise consolidate as glass. Thus tungstates facilitate the crystallization of orthoclase, albite, and leucite. This influence is held by some to support the theory of mineralizers (*agents minéralisateurs*),[3] and it is certain that the curves of crystallization tendency and velocity are modified by the presence of such substances. Magmas, also, must often vary considerably in viscosity in different parts. Local richness in water vapour or other volatile fluxes may explain those variations of texture which are independent of the cooling surfaces. The rarity of glassy forms in plutonic rocks may be attributed to the influence of magmatic water and other mineralizers, combined with slowness of cooling through the temperature range where crystallization can take place.

Glassy Structures.—Since viscosity increases as the temperature falls, the formation of glassy structures should be promoted by the complexity of the magma, for complex magmas have, as a rule, low melting points. For the same reason, as crystallization proceeds, the greater will be the viscosity of the residual mother liquor. If, therefore, the rate of cooling is greater than the time required for crystallization, a glass basis will be formed.

Vogt found that slags possessing the composition

[1] Amer. Journ. Sci., xix. 93 *et seq.*, 1905.
[2] *Loewinson-Lessing*, Centr. f. Min., p. 288, 1900.
[3] *Doelter*, Physikalisch-Chemische Mineralogie, pp. 109, 113.

of a pure mineral, such as anorthite, or a member of the akermanite-melilite-gehlenite series, will crystallize completely, even if quickly cooled. But if both are present, the melting point is lowered. If they are present in nearly eutectic proportions, the lowering of the melting point may be so great that a glassy mass is formed, unless the time of cooling is greatly prolonged. For this reason many glasses are believed to be of nearly eutectic composition.[1] The composition of a magma may also exert an influence upon the formation of glass on cooling. Vogt has stated that the presence of alumina has the effect of promoting glassy structures.[2] He attributes this partly to a lowering of the melting point and partly to an increase of viscosity due to its presence. Morozewicz, however, maintains that the behaviour of alumina is explained by the fact that it requires a large excess of this substance to saturate magmas, and to separate in the form of corundum or sillimanite. A small excess only serves, in his opinion, to form unsaturated solutions, and, in consequence, solid solutions or glasses.[3]

This suggests the possibility that some of the residual glass in volcanic rocks may owe its formation to its composition. Just as devitrification takes place much more readily in some glasses than in others, so the inverse process may vary also. Darwin long ago referred to the possibility of a separation of heavy crystals from a magma by sinking, whereby an upper magma might be left with a composition which, even by slow cooling, might form obsidian.[4] Although this view has not been generally accepted, yet the mode of occurrence of some glassy rocks is difficult to reconcile

[1] *Lagorio*, "Über die Natur des Glasbasis," Tschermak. Min. u. Pet. Mitt., viii. 421 *et seq.*, 1887.
[2] *Op. cit.*
[3] Tschermak. Min. u. Pet. Mitt., xviii. 1-240, 1898.
[4] Volcanic Islands, p. 117, 1844.

with the view that these have been rapidly chilled. Thus, although glass often forms a selvedge on the chilled margin of an igneous intrusion, it occasionally occurs inside the mass. In the Eskdale Dyke, in Dumfriesshire, glass segregates in the irregular patches and bands within the mass,[1] and in the Tynemouth Dyke and in the Beinn Hiant rocks it has been squeezed into gas cavities and other spaces within the mass.[2] Such glasses may possibly possess a composition which does not admit of separation into stoichiometric components.

We may now examine the problem from the point of view of devitrification. Glasses are, as already

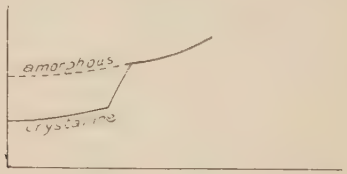


FIG. 6.—DIAGRAM ILLUSTRATING THE VARIATION OF ENERGY IN THE CRYSTALLINE AND AMORPHOUS STATES.

explained, supercooled liquids, in which the tendency towards crystallization is held in restraint by viscosity. Increase of temperature diminishes viscosity, and may enable crystallization to take place. Even in the absence of any increase of temperature, the process of crystallization may proceed slowly. For this reason, true glass is rarely found in the older rocks of igneous origin. Most silicate glasses, therefore, appear to be in a condition of false equilibrium. They possess a higher thermo-dynamic potential than the crystalline form, and their relative energy isobars may be represented as in the accompanying diagram (Fig. 6).

[1] *Geikie*, Trans. Roy. Soc. Edinb., xxxv. 40-44, 1888.
[2] *Teall*, Geol. Mag., pp. 481-483, 1889.

The greater energy of the amorphous phase under normal conditions has been experimentally verified by Lemberg, who has shown that glassy silicates are more readily decomposed by saline solutions or acids, and possess higher electric conductivity than the crystalline forms.[1] The case of borax glass is instructive in this connection, because until recently all attempts to induce crystallization in a slowly cooled mass of this substance were unsuccessful. Tammann, therefore, considered this a typical case of a stable amorphous phase. Day and Allen, however, have lately succeeded in producing the crystalline phase of fused borax glass.[2]

The facility with which devitrification can be induced in glasses, either by diminishing their viscosity by heating, or by slow changes at ordinary temperatures, varies much in glasses of different compositions. Thus, potash glasses devitrify more slowly than soda glasses. Glasses rich in lime and magnesia are very readily devitrified, and generally the process is assisted by the presence of finely-divided refractory matter capable of serving as nuclei.[3]

Pressure would be expected to promote devitrification, because the crystalline phase has the smaller volume.

Amorphous matter often passes spontaneously into a crystalline condition. The crystallization of amorphous precipitates is a familiar laboratory phenomenon. In Nature it is difficult to point to unequivocal examples of this tendency on account of the impossibility of eliminating the influence of moisture.

Perman has shown how important is the effect of even small quantities of water in determining chemical

[1] Zeit. d. Deut. Geol. Gesell., p. 587, 1887; pp. 626, 637, 1888.
[2] Amer. Journ. Sci., xix. 93, 1905.
[3] A state of strain is favourable to devitrification, as proved by the influence of annealing.

changes.[1] The process, therefore, by which amorphous sedimentary rocks pass into a crystalline condition can scarcely be called examples of equilibria in univariant systems. In all such cases the crystalline state may be the result of solution, and not a spontaneous transition from an amorphous to a crystalline form. Holland has recently suggested that in certain cases the force of crystallization may be sufficiently great to overcome the force of chemical affinity, and he thus explains the spontaneous crystallization of hematite at the expense of amorphous limonite.[2] A somewhat analogous case of spontaneous crystallization has been described by Miers.[3] The gold occurring in the pyrites of the Ural Mountains is uniformly disseminated, but when the pyrites weathers to limonite, the gold forms nuggets with crystalline faces. In the absence of a solvent for gold this might indicate a certain crystallization force in the released gold, but the possibility exists of crystallization from solution in ferric sulphate. The influence of solvents is all the more probable on account of the more ready solubility of the amorphous phase in consequence of a higher energy of reaction.

Viscosity and Diffusion.—Knowing the diffusion constant K of a liquid, its frictional resistance may be calculated by Nernst's formula:

$$R = \frac{1 \cdot 99}{K}(1 + 0{\cdot}00367t) \times 10^9.$$

From this it is seen that the speed of diffusion is inversely proportional to the viscosity. If we imagine a small spherical particle moving without turbulence in a viscous fluid, the force resisting its motion can be shown to be $6\pi\eta a V$, where $a$ is the radius of the particle, V its velocity, and $\eta$ is the viscosity coefficient of the medium. Viscosity, therefore, will retard diffu-

[1] Brit. Assoc. Rep., Section B, 1903; Chem. News, p. 197, October 30, 1903.

[2] Geol. Mag., x. 67, 1903.

[3] Brit. Assoc. Rep., p. 561, 1904

sion in proportion to the molecular volume of the diffusing substances. This consideration may be of some importance in connection with rock magmas. The molecules being of different sizes, viscosity will check the larger ones to a greater degree than those of smaller volume.

Viscosity has often been urged as a difficulty in the application of diffusion to rock magmas. It is necessary, however, to draw a distinction between the more viscous condition of magmas and the more fluid condition under which they may exist in plutonic regions, where viscosity is diminished by high temperatures, and by the presence of magmatic water, and where diffusion can take place with greater freedom. As has already been stated, magmas differ greatly in viscosity even when extruded. The more fluid basic magmas spread out over wider areas than the more viscous acid magmas. Segregation and diffusion phenomena become less pronounced as viscosity increases, and differentiation becomes less perceptible as the molten material assumes a pasty condition.

This also has a great influence upon the phenomena at the contact zone. Let us take, for example, the suspension and assimilation of zenoliths. Theoretically the specific gravity of most solid rocks is greater than that of magmas, yet basic zenoliths are found suspended in acid igneous rocks. Daly has considered this question in detail. Excluding the influence of viscosity, he finds that: (1) A solid block of any igneous rock should sink in its own magma; (2) blocks of basic rock should sink in all magmas except the more basic gabbros and peridotites; (3) the heavier granites and syenites should also sink in any magma with these exceptions; (4) all average sediments and schists should sink in any magma with the same exceptions; (5) sandstones and argillites should float in magmas

of the density of syenite; (6) the lighter gneisses, quartzites, and many limestones should only float in an average gabbro magma. Such speculations, however, are more applicable to plutonic magmas in a highly fluid state.[1] The phenomena observed at contact zones show that the viscosity of the magma may not only allow zenoliths to remain near the place of their detachment, but may also often prevent any appreciable corrosion. Where partial assimilation has taken place, the more refractory minerals, such as quartz and acid felspars, often remain as zenocrysts. Brögger noted the universal connection, in the Christiania district, between marginal differentiation in the intrusion and marked contact metamorphism in the country rock.[2] It would be expected that the separation of a marginal facies would be related to the length of time during which the magma retained a high degree of fluidity, and would, therefore, be in inverse proportion to its viscosity.

Viscosity also explains the persistence of streaks, or "schlieren," without appreciable admixture with the magma by diffusion. To increasing viscosity, also, must be ascribed the sudden falling off in intrusive energy which dykes occasionally display. Harker has described striking examples of this kind, and he is inclined to think that this fact may occasionally invalidate arguments respecting the age of an intrusion which are based upon the non-penetration of certain rocks.[3] This feature is well illustrated in the Monzoni district, where the camptonites, melaphyres, and augite-porphyrites penetrate freely into the smallest cavities in the contact rocks, while the apophyses of the acid rocks are stumpy and deficient in penetrating power.

[1] See *Daly*, "The Mechanics of Igneous Intrusions," Amer. Journ. Sci., xv. 269 *et seq.*, 1903.

[2] Ganggefolge des Laurdalits, p. 334 *et seq.*

[3] Tertiary Igneous Rocks of Skye, p. 432.

## III

### DIFFUSION AS A FACTOR OF EQUILIBRIUM CONDITIONS

Diffusion plays an important part in geological processes. Gaseous diffusion is concerned in all pneumatolytic phenomena, and influences the amount and nature of the alterations produced by the action of vapours and gases at the contact zone of igneous and sedimentary rocks. Liquid diffusion is responsible for the migration of dissolved matter, and tends to maintain a uniform concentration in the solutions percolating through the earth's crust. It also determines the equilibrium conditions of molten magmas. Solid diffusion, although a more obscure phenomenon, is now accepted as a physical fact, and assists in explaining many kinds of mineral transformations.

Diffusion of Gases.—Diffusion of gases and vapours depends upon the kinetic principle of molecular bombardment. This action is governed by Graham's law, which states that the volume of a gas which passes through a porous plate in a given time is directly proportional to the difference of the pressures of the gas on the two sides of the plate, and is inversely proportional to the square root of the molecular weight of the gas—that is to say, the rate of diffusion is proportional to the average velocity of translation of the molecules.

In geological processes the most important case to

consider is the passage of gases and vapours through the exceedingly fine pores of rocks and minerals. It has been demonstrated that a mixture of two gases penetrates plates of meerschaum or graphite each independently of the other, and the composition of the mixture is changed by the process of diffusion. The partial separation of a mixture of gases which can thus be effected, known in physics as atmolysis, probably exerts an influence in all pneumatolytic actions that take place in rocks. The change in concentration in gases and vapours, differing in density, which can thus be produced, may be considerable. The same law will apply to the vapour phase of solids and liquids, and will facilitate the separation of the lighter and heavier molecules. Increase of temperature promotes diffusion not only by increasing the molecular activity of gases and vapours, but by increasing the porosity of the solid through which diffusion takes place. Thus Deville and Troost found that quartz at high temperatures permits the passage of the gases of the oxy-hydrogen flame, and hydrogen penetrates readily through red-hot platinum and iron. Under the influence of the electric current, lithium, with an atomic volume of 15·98 could be made to pass along the tracks or molecular galleries left in glass by the escape of sodium atoms, having an atomic volume of 36·04; but potassium, with a larger atomic volume, would not thus chase out the sodium atoms from glass.[1] This phenomenon may have some bearing upon the penetration of molecules into minerals. Thus Becker describes clastic quartz grains in which long, slender microliths of serpentine stick like pins in a cushion.[2] Similar penetrations are familiar occurrences in petrographical geology, but care is necessary in discriminat-

[1] Wied. Ann., xli. 1-41, 1890.
[2] Mon. U.S. Geol. Surv., xiii. 124, 1888.

ing actual penetrations from secondary growths of the host around the included mineral.

Diffusion of Solids.—The diffusion of solids has been investigated by Daniell,[1] Henry,[2] Roberts-Austen,[3] Spring,[4] and others. At ordinary temperatures the action is extremely slow. Thus, the rate of diffusion of gold into lead under these conditions would take 3,000 years to produce a result which would be accomplished in a single day if the metals were in a molten state. At a temperature of 500° C., however, the rate of diffusion of gold into lead appears to be greater than that of sodium chloride through water at 18° C. The diffusion of carbon into iron, also, in the cementation process of steel manufacture is enormously facilitated by heat.

Solid diffusion has hitherto only been recognized in laboratory experiments between metallic solids which exert a solvent action upon each other, and have, moreover, an appreciable vapour pressure. The vapour pressure of the more volatile metals, such as mercury and zinc, is considerable even at ordinary temperatures. Gold-leaf suspended near mercury becomes amalgamated in a short time. It is possible, therefore, that what has been described as the diffusion of solids is merely a diffusion of vapours. Greenly's suggestion of a diffusion of granite into surrounding Highland schists, after the consolidation of the igneous rock,[5] presents many difficulties. The fundamental principle of diffusion seems to preclude the possibility of the diffusion of the molecules of the components of granite at equal rates; and the suggestion, also, that extensive molecular changes in solid rocks may be due to solid diffusion, although not im-

[1] See *Poynting* and *Thomson*, Properties of Matter, p. 204.
[2] *Ibid.* [3] Phil. Trans. A., clxxxvii. 393, 1896.
[4] Zeit. f. Phys. Chem., xv. 76, 1894.
[5] Geol. Mag., x. 212 *et seq.*, 1903.

possible, has to encounter the difficulty that a change of this kind could only take place from the surfaces of minerals in contact, and the complete alteration of large crystals in this way is not easily conceivable without the intervention of matter in solution or in the vapour phase. A further objection to such a view is furnished by the sharpness of the boundary lines of zoned crystals, such as many kinds of garnet, tourmaline, and augite, in which no trace of diffusion can be traced after intimate contact for geological ages. The observations of Trener,[1] also, with respect to the contact phenomena of the granite of Cima d'Asta, ascribed by him to solid diffusion from the periphery of the granite into the surrounding schists, can possibly be explained by liquid or gaseous diffusion prior to complete consolidation.

So far as experimental evidence goes, therefore, the so-called solid diffusion may merely indicate that those solids which exhibit this property have an appreciable vapour tension. The laws of gaseous diffusion would then apply.

Diffusion in Liquids.—Osmotic pressure is generally accepted as the cause of diffusion in liquids. The intensity of osmotic pressure is certainly great enough to account for diffusion. In the case of a strong solution of cane-sugar the osmotic pressure has been found to exceed 100 atmospheres, and the osmotic pressure of a 1 per cent. solution of auro-potassic cyanide is 12·2 pounds per square inch.

There is some difference of opinion as to the cause of osmotic pressure. The analogy between osmotic pressure and gas pressure, suggested by Van 't Hoff, has been since found to be not quite in accordance with experimental results, which are believed to support rather the theory that equality of vapour pressure

[1] Verh. Geol. Reichanst, Wien, pp. 366-370, 1905.

accounts better for osmotic equilibrium. It can be shown that even minute differences of vapour pressure can produce these effects.[1] Other explanations have been proposed by Kahlenberg, Beilby, and others, but these depend upon a distinction between solvent and solute, and introduce unnecessary complications. Another view of osmotic pressure, due to Traube, attributes all such phenomena to differences of surface tension. This view has recently been advocated by Battelli and Stefanini.[2] These observers find that solutions having the same surface tension are always in osmotic equilibrium, even although they are not equi-molecular. They conclude that osmotic pressure is not a purely kinetic phenomenon.

Fick's law appears to hold for all those cases of liquid diffusion that have been experimentally investigated. This law may be enunciated as follows :

$$\frac{dc}{dt} = k \frac{d^2c}{dx^2},$$

where $x$ is the distance through which diffusion takes place against gravity, $c$ is the concentration of the diffusing substance in gramme molecules per cubic centimetre, $t$ is the time of diffusion, and $k$ is the diffusion constant — *i.e.*, the number of grammes diffusing per square centimetre in a unit of time, when unit difference in concentration is maintained between layers 1 centimetre in thickness.

This equation shows that the speed of diffusion varies directly with the concentration, and inversely as the square of the distance. The value of the diffusion constant varies in different substances. Diffusion is very slow even in liquids of small viscosity. Thus, a tube 1 metre long, the lower half of which is filled with a saturated solution of copper

[1] *Callender*, Nature, p. 235 *et seq.*, August 19, 1909.
[2] Physikalische Zeitschrift, March 15, 1906.

sulphate, and the upper half with pure water, would take ten years to mix uniformly. The motive power may be partly due to the osmotic pressure gradient and partly to the electric forces between the ions. This explains why the diffusion of electrolytes is more rapid than that of non-electrolytes. Solutions possessing great electric conductivity, such as molten metals, diffuse with comparative rapidity. The rate of diffusion is, however, greatly retarded by viscosity. Thus, if a few pounds of ferro-manganese are thrown into ten tons of molten iron, the resulting ingots are approximately uniform in composition. On the other hand, in the manufacture of optical glass it is found extremely difficult to secure perfect homogeneity, even when diffusion is assisted by stirring, or by promoting convection currents by heat. The action of stirring enormously increases the speed of diffusion by producing thin layers of different concentrations in contact with one another.

Generally, solutions are only in equilibrium when under uniform osmotic pressure. Such solutions are said to be isotonic. When from any cause solutions are not isotonic, diffusion tends to restore equilibrium.

Diffusion in Rock Magmas.—In applying the laws of diffusion to rock magmas, the ordinary conception of the process seems difficult to state. In physics liquid diffusion usually postulates a distinction between solvent and dissolved substance. This distinction has also been attempted in the case of magmas,[1] but it involves a difficulty in determining which constituent should be regarded as the solvent. It seems preferable, therefore, to regard fused salts in the same light as molten alloys—*i.e.*, as reciprocal solutions, in which

[1] *Vogt*, Zeit. f. Prakt. Geol., p. 329, 1901; *Brögger*, Ganggefolge des Laurdalits, p. 356; *Loewinson-Lessing*, Centr. f. Min., ix. 288, 1900; *Doelter*, Tschermak. Min. u. Pet. Mitt., xxi. 223.

any of the constituents may be looked upon as the solvent of the others. The distinction between solvent and dissolved substance is not necessary even for aqueous solutions. As regards diffusion, the molecules may be regarded as acting independently, in the same way as mixtures of gases and vapours, each molecule moving with a velocity depending upon its molecular activity towards a state of isotonic equilibrium.

Very little is known with regard to the ionization of fused silicates, upon which, as has been shown, the rate of diffusion partly depends. It is not known whether the electric conductivity of fused salts is due to a few ions moving with a high velocity, or to many ions moving with low velocities.[1] Compared with aqueous solutions, the conductivity of magmas increases very rapidly with rise of temperature, and often exceeds that of the best conducting aqueous solutions.[2]

It has also been established that fused salts follow Faraday's laws of electrolysis,[3] apparent exceptions being due to the diffusion and recombination of the products of electrolytic decomposition. While, therefore, it seems probable that in magmas of high fluidity and temperature the diffusive power may approximate to that of molten metals, precise knowledge upon this point is still wanting.

The question of diffusion in magmas assumes particular importance in geology from two opposite points of view. Viewed generally, diffusion would be expected to promote homogeneity. It is, however, to explain heterogeneity that this agency has been largely advocated. From this standpoint, diffusion may be

[1] *Lehfeldt*, Electrochemistry, p. 90, 1905.
[2] *Kramers*, Arch. Néer., i. 455-494, 1896.
[3] *Lorentz*, Zeit. f. Electrochem., vii. 277-287, 1900; viii. 750.

considered with reference to the power of molten rock to assimilate and absorb foreign matter, such as the walls of the country rock; or it may be considered with regard to the origin of border segregations and contact phenomena produced during the cooling of an intruded mass. It will be convenient to consider the latter first.

Soret's Hypothesis.—An osmotic pressure gradient is set up in any magma in which the temperature is not uniform. This follows at once from the fact that osmotic pressure is proportional to the absolute temperature as well as to the concentration. Hence in the cooler parts of a magma the osmotic pressure will be less than in the warmer parts. Thus equilibrium will be destroyed, and there will be a tendency for the molecules to concentrate in the cooler parts to restore equilibrium. That such a result takes place in aqueous solutions was first proved by Ludvig in 1856.[1] Later, Soret investigated the case of a copper sulphate solution, one portion of which, cooled to 20° C., contained 17·332 per cent. of the salt, whereas the hot portion, at a temperature of 80° C., contained only 14·02 per cent.[2]

In an isotonic liquid the product of the absolute temperature and the concentration must be equal in the hot and cold parts. Now $(273+20)\ 17{\cdot}332 = (273+80)x$; whence $x = 14{\cdot}3$. Thus the theoretical result nearly agreed with that obtained by experiment. At higher concentration Soret obtained more than the theoretical difference. The restoration of equilibrium was extremely slow, and after fifty-six days only one-third of the concentration in the cold portion required for an isotonic state was produced.

This result, commonly known as Soret's principle

[1] Berichte, xx. 539, 1856.
[2] Ann. de Chim. et de Phys., xxii. 293, 1881.

has been widely discussed in connection with the local differentiation often observed in the marginal portions of igneous intrusions, to the explanation of which it was originally applied by Lagorio, and subsequently by Teall, Brögger, and others.

The fact is clearly established that the minerals of early consolidation are sometimes concentrated in the marginal parts of igneous masses. The phenomenon has been more noticed in basic than in acid intrusions, which may, perhaps, be due to the retention for a longer time of a condition of high fluidity in the former; whereas in the latter viscosity quickly supervenes on cooling.

The fact that border segregations always concern the minerals of early consolidation, and not those of greatest relative concentration, is significant. If the molecules in solution in magmas obey the laws of gaseous diffusion, then their relative rates of diffusion would be expected to vary directly as the concentration, and inversely as the square root of their density. Theoretically, therefore, the margins would be expected to show a concentration of those molecules which are present in the greatest proportion in the magma. By carefully adjusting the concentrations in the original solutions, with due regard to the relative mobilities of the molecules, the cooler portion could be made to show a relative excess of either component. In a cooling magma, however, crystallization is going on at the margins, and the more insoluble molecules are being continually withdrawn from the solution, thus increasing the osmotic pressure gradient for these molecules. Thus, the molecules which crystallize first will also diffuse most rapidly, because their osmotic pressure gradient is kept steep by the continual removal of molecules from solution. This explains why the segregated minerals are those of the first

stages of crystallization. If a barrel of cider is frozen from the outside, ice will form around the margins, and the interior liquid will increase in alcoholic strength. The osmotic pressure gradient is in this case inwards for the alcohol molecules. If the cooling faces could be kept for a prolonged period at a temperature just above the crystallization temperature of the minerals in the magma, the final result would be that the magma would become isotonic for the whole of the constituents, and would then have the same relative concentration throughout, but different absolute concentrations in the warm and cool parts respectively. It is possible that this condition may arise in some cases. More often, however, the temperature falls rapidly to a point at which diffusion is checked by viscosity. The existence of a border facies, therefore, is evidence of such a rate of cooling that while crystallization was proceeding at the margin, the inner parts retained a high degree of fluidity. This is supported by Brögger's observation that the most differentiated igneous masses show the most marked contact effects upon the surrounding rocks. Harker's objection[1] that the amount of segregated material at the margin is out of all proportion to any conceivable difference in temperature between the central and marginal parts, loses its force in the light of the above argument. There could be no proportionality unless equilibrium were established before consolidation began. Progressive crystallization removes the segregated molecules from the sphere of action as fast as they arrive at the margin. A considerable amount of the solid might, therefore, accumulate without any very great difference in concentration at any particular stage of the process, between the central and peripheral parts of the still fluid magma. In this connection it

[1] Geol. Mag., x. 546, 1893.

may be mentioned that Payen has described the experimental formation of a sahlband.[1]

It would be expected that if diffusion plays so important a part in marginal differentiation, the later stages of consolidation will be more homogeneous than the earlier stages. This is often the case.[2] The check to the progress of diffusion caused by increasing viscosity may occur suddenly, in which case there will be a sharp boundary between the marginal facies and the central rock, as is seen in the quartz porphyry dykes of Christiania, and in the Square Butte laccolite. More often, however, there is a gradation from margin to centre, showing that the increase of viscosity took place very gradually.

The process of diffusion is hastened by convection currents, as Becker has suggested. Such currents act as stirrers.[3]

Influence of Gravity.—In laboratory experiments, the influence of gravity upon the conditions of equilibrium required by the laws of diffusion is generally extremely small. This question has been considered in detail by Gouy and Chaperon.[4] They conclude that, from thermo-dynamical considerations, the final state of equilibrium in solution is not one of perfect homogeneity, but that the density increases from top to bottom according to a definite law. Upon this supposition the theoretical concentration of sea salt at the surface of the ocean will be 0·0005 less than at a depth of 100 metres. They conclude that in a very large mass of solution the conditions of equilibrium will result in a progressive concentration of the heavier molecules towards the bottom, causing a process of differentiation to take place.

[1] Journ. f. Prakt. Chem., lvi. 319, 1852.
[2] *Harker*, Quart. Journ. Geol. Soc., l. 328, 1894.
[3] Amer. Journ. Sci., v. 353, 1898.
[4] Ann. de Chim. et de Phys., xii. 384, 1887.

The possibility of the application of this theory to the differentiation of igneous magmas has been denied by Lehmann, who maintains that, so long as a solution maintains in all parts the same temperature, and none of the solvent is removed, gravity can produce no change in its homogeneity; but if, from any cause, a separation takes place into solid and liquid, or imperfectly miscible liquids, then gravity will operate to produce further separation.[1]

A difficulty in the application of Gouy and Chaperon's theory to differentiation in magmas is that any separation from this cause must be progressive, and the depth of the magma basin in which differentiation into distinct acid and basic types of rock could thus be produced would have to be considerable.

The circumstances are quite different, however, if crystallization has already begun to take place, when a separation by gravity may occur. In this way, Loewinson-Lessing explains the floating up of large leucite crystals to the surface of Vesuvian lavas,[2] and the sinking of augite crystals to the lower parts. Such a process may explain the various modifications of augite porphyrite, which are sometimes rich in felspar, and at other times in augite. Harker thus accounts for the occasional presence of quartz in the so-called quartz basalts.[3] Scrope long ago suggested the possibility of the separation of heavy from light minerals in this manner,[4] and his view has been supported by various writers. Popow thus explained the distribution of the spheroidal concretions in the granite of Rappakiwi,[5] and Collomb maintained that the orbicular masses in Corsite floated up in a liquid

[1] Molekularphysik, i. 483.
[2] Studien über die Eruptivgesteine, p. 155.
[3] Geol. Mag., p. 485, 1872.
[4] Volcanoes, p. 125, 1872.
[5] Arb. d. St. Petersb. Naturf. Gesell., 1877.

or pasty bath.[1] De Lapparent, also, found the lavas of Teneriffe and Guadeloupe to be in three layers, in the order of their acidity.

While, however, by the sinking of heavy minerals, or by the rising of minerals lighter than the magma, a differentiation by gravity may take place, this is a process quite distinct from the separation of fluid molecules in accordance with the principle of Gouy and Chaperon. There is at present no proof that the latter process is alone capable of producing a separation by gravity into distinct layers in the same sense as the theories of Von Waltershausen and Durocher require. In the case of fluids which do not mix, a separation by gravity always occurs. Several examples of such non-consolute liquids are known in the laboratory. Loewinson-Lessing and others strongly advocate the hypothesis that liquids which are consolute at certain temperatures and concentrations may become non-consolute at other temperatures and concentrations. This theory would, it is true, account for many of the phenomena ascribed to this process. Its supporters, however, appear to overlook the fact that the process, in its physical sense, involves complete diffusion, since before a separation can take place the mixture must reach a definite homogeneous composition. It involves the same difficulties, therefore, as those which depend purely upon diffusion.

The Assimilation Hypothesis.—So far diffusion has been considered with regard to equilibrium between the component parts of one and the same magma. It remains to examine the conditions that may result from the reaction of a magma upon the invaded rock. Some geologists maintain that the rate of diffusion is too slow for any appreciable differentiation to result from this cause. It is claimed that the

[1] Bull. Soc. Géol. de France, xi. 63, 1853-54.

marginal phenomena of igneous intrusions is to be explained, not by an endogenous, but by an exogenous process, involving an absorption of country rock.

The modification of magmas by assimilation of invaded rock may be considerable in deep-seated regions where the temperature is high; but positive evidence of any extensive action of this kind in igneous contacts accessible to observation is by no means abundant. The completeness of such a digestion of foreign matter must depend primarily upon the temperature of the magma and the rapidity of diffusion, aided by convection currents and mechanical mixing, due to magmatic movements. It has been claimed by Michel Lévy, Barrois, Lacroix, Johnston-Lavis, Sollas, Cole, and others, that such a process has taken place to a considerable extent. Barrois maintains that the granites of Brittany show real deep-seated phenomena of this kind. Lacroix has described similar phenomena in the Pyrenees. Doelter finds a confirmation of this view at Monzoni, in the Tyrol. Sollas comes to a similar conclusion with regard to the granite of Barnavave, and Cole thus explains the structure of Slieve Gallion.

Extreme views of this process have been advanced by Daly and also by Goodchild. Daly assumes an extreme fluidity in the more deep-seated regions. Igneous intrusions, he contends, make their way through the solid rock by a process of overhead stoping. The solid blocks thus torn off in most cases gravitate to the bottom, and are there absorbed. In a later paper he describes cases in which basic rocks, such as olivine gabbro, appear to have been acidified by the assimilation of acid rocks, so as to become granite. Goodchild maintained that a more or less complete assimilation of country rock takes place immediately. He likened the process to what takes

place when a fragment of more fusible metal is placed in a molten mass of less fusible metal. In the case where the two metals readily form an alloy, diffusion is complete without mechanical aid. He has thus accounted for the uniformity of composition of intrusive rocks, even when they invade solid rocks of very diverse composition.

An extensive assimilation of the invaded rock has also been advocated by Loewinson-Lessing, who suggests that the magma, owing to the well-known laws governing the melting-point depression, would become more fluid as a result of the digestion of foreign material, by which diffusion would be facilitated. Another view of the assimilation theory has been advanced by Johnston-Lavis. This he describes as the osmotic theory, which assumes a partial digestion and lateral absorption of the country rock by an osmotic process.[1]

The great difficulty in all these theories is the large amount of heat which would be required to cause the fusion and absorption of solid rocks in the upper parts of the earth's crust. Many fundamental objections, also, may be based upon observed phenomena. Brögger has examined this theory in detail.[2] There are many cases where the transfer of material can be shown to have been quite insignificant.[3] Geological literature contains innumerable examples bearing upon this question, and the mass of evidence cannot be said to support the view that assimilation or transfer of material has been extensive or general.[4]

[1] Natural Science, iv. 134, 1894.

[2] Ganggefolge des Laurdalits, p. 341.

[3] *Harker*, Quart. Journ. Geol. Soc., xlix. 368, 1893; *Barrell*, Amer. Journ. Sci., xiii. 290, 1902; *Weed*, Twenty-first Report U.S. Geol. Surv., p. 400.

[4] *Lindgren*, Trans. Amer. Inst. Min. Eng., September, 1904; *Klockmann*, Zeit. f. Prakt. Geol., xii. 78, 1904; *Vogt*, Trans. Amer.

Diffusion, moreover, in this case presents quite as many difficulties as in the case of other views of the origin of differentiation phenomena. At the same time, it is certain that assimilation has sometimes taken place to a limited extent. The observations of Lacroix on the contact phenomena near the junction of granite and limestone in the Pyrenees show that included lenticles of limestone are surrounded by zones of modified granite, which become in places more basic in character and give place to diorite and even to norite and hornblende peridotite.[1]

Coming next to the power of magmas to assimilate other magmas, Bunsen long ago suggested that intermediate rocks might be formed by an intimate mixture of extreme types. Such an intermingling of magmas of various compositions does probably take place under certain conditions, but surface observations do not always lend support to the view. Harker, who has examined certain cases of apparent magmatic mixtures, finds that the results of such a process are hybrid rocks of essentially abnormal types.[2] Of this nature is marscoite, a rock resulting from the juxtaposition of acid and basic magmas.[3]

There are many examples of basic rocks veined and brecciated by acid material, and *vice versâ*, forming banded gneiss and other types of rock, and it is necessary to conclude that under certain conditions magmas of different kinds can coexist for a time without any appreciable blending by diffusion. An intimate intermixture, resulting in complete blending of the two rocks, is, however, not unknown, as, for example, in

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Inst. Min. Eng., p. 648, 1902; *Weinschenck*, Zeit. d. Deut. Geol. Gesell., liv. 443, 1902.

[1] Bull. des Services de la Carte Géol. de la France, x. 19-24.

[2] Journ. of Geol., viii. 389, 1900.

[3] Tertiary Igneous Rocks of Skye; also Natural History of Igneous Rocks, p. 357.

the contact zone between the gabbro and granophyre of Carrock Fell.[1] In the many known cases of composite dykes, even where there is evidence of a partial liquefaction of the earlier intrusion, diffusion has been comparatively slight; in fact, abruptness of transition is a characteristic of composite dykes, and serves as a main point of distinction between them and differentiated dykes with pronounced although graduated sahlbands.[2]

Lastly, there are often to be seen, in the midst of igneous masses, basic secretions, "schlieren," and other phenomena, which are difficult to explain if diffusion had been active. The evidence of diffusion in rock magmas is of a contradictory nature. The cause of this apparent discordance is probably to be found in the influence of viscosity in preventing the establishment of true equilibrium.

[1] *Harker*, Quart. Journ. Geol. Soc., l. 330, 1894.

[2] *Judd, ibid.*, xlix. 539, 1893; *Lawson*, Amer. Geol., vii. 153-164, 1891; *Vogt*, Zeit. f. Prakt. Geol., i. 4, 1892; *Geikie*, Quart. Journ. Geol. Soc., lii. 394, 1896; *Harker*, Tertiary Igneous Rocks of Skye, chap. xii., etc.

## IV

### SURFACE TENSION AS A FACTOR OF EQUILIBRIUM

The absence of cohesive attraction on the outside of the superficial layer of a substance must result in a relatively greater stability of position of its molecules with reference to movement outward from the mass, and a tendency to diminish the extent of surface as a resultant of cohesive forces acting from within. This molecular condition prevailing at the free surface of a body is called surface tension. A body free from the influence of other forces, capable of overcoming surface tension, will assume a shape which makes the surface energy a minimum. This is in accordance with the universal law of equilibrium, which states that the thermo-dynamic potential constantly tends towards zero. Any change which promotes a decrease in this portion of the energy of a system, if it does not increase other parts of the energy, will, therefore, tend to occur.

Surface tension is one of the most important factors in supersaturation conditions. Thus, air may remain supersaturated with water vapour in the absence of nuclei.[1] The function of these nuclei is to diminish the surface energy by increasing the size of the products of condensation. Spontaneous precipitation of water vapour is rendered difficult on account of the enormous quantity of free energy required for the formation of minute drops.

[1] *Aitken*, Trans. Roy. Soc. Edinb., xxx. 337, 1881

In the case of two liquids which do not mix, it is easy to determine the conditions under which one liquid, A, will spread over the surface of another liquid, B, or will gather into drops. That result will follow which involves a decrease in the potential energy of the system.[1]

We may consider the three tensions $T_1$, $T_2$, $T_3$, where $T_1$ is the tension between A and air, $T_2$ that between B and air, and $T_3$ that between A and B. If now the surface of contact between A and B is increased by an amount S, then the energy of surface tension between A and B is increased by $T_3S$, that between A and air is increased by $T_1S$, and that between B and air is diminished by $T_2S$. The total change of surface energy of the system is, therefore, $(T_1 + T_3 - T_2)S$.

If this is negative—that is, if $T_2$ is greater than $T_1 + T_3$—then A will spread over B; but if any one of these three terms is less than the other two—that is, if Neumann's triangle can be constructed—then A will not spread, but a drop of one liquid can exist on the surface of the other. In all cases which have been investigated Neumann's triangle cannot be drawn. Some apparent exceptions are due to the fouling of the surface of one of the liquids. Thus, Quincke has shown that a drop of pure water will spread over pure mercury.

In the case of a solid in contact with a liquid and air, there is equilibrium at the meeting point of three surfaces. The angle of contact between the solid and the liquid is determined by the equation:

$$\cos\theta = \frac{T_1 - T_3}{T_2},$$

where $T_1$ and $T_2$ are the surface tensions beween air and the solid and liquid respectively, and $T_3$ is the surface tension between the solid and the liquid.

[1] *Poynting* and *Thomson*, Properties of Matter, p. 135 *et seq.*, 1902.

For wetted surfaces $\theta = 0$, and $\cos \theta = 1$; then $T_2 = T_1 - T_3$. The values of $T_1$, $T_2$, and $T_3$ vary with the nature and concentrations of the substances

In the case of fused minerals this is well illustrated by the experiments of Joly on the determination of fusion points by means of the meldometer. Fused apatite immediately runs up a platinum wire, as also does olivine; but orthoclase remains as a spherical globule, and basalt retains a globular shape until the highest temperature is attained.[1] In all cases the conditions of equilibrium are determined by the value of $\cos \theta$ in the above equation.

The influence of the shape of the surface of contact has been investigated by Hulett,[2] who finds that the concentration of a solution in equilibrium with a curved surface is different from that in equilibrium with a plane surface. A normally saturated solution is the solution in equilibrium with a plane surface. A convex surface was found to have a greater solubility, and a concave surface less solubility than the normal. These observations are of interest, as will be seen, in connection with the growth of crystals.

The surface tension of all liquids diminishes with increase of temperature. The rate of decrease has been given by Eotvos in terms of the molecular volume ($v$) of the liquid by the formula—

$$\frac{d(Tv^{\frac{2}{3}})}{dt} = -2{\cdot}1,$$

where T is the surface tension and $t$ is the temperature.

Application of the Principle of Surface Tension.—The variation in the surface tension of minerals has been turned to account in the process of separating ores by means of oil.[4] Certain sulphides are more

[1] Trans. Roy. Dub. Soc., vi. 283, 1897.
[2] Zeit. f. Phys. Chem., xxxvii. 385, 1901.
[3] Wied. Ann., xxvii. 448, 1886.
[4] *Hamilton*, Journ. Can. Min. Inst., vii. 185, 1905.

readily wetted by oil than by water, and when in contact with both liquids, the oil seizes the sulphide ores and floats them away from the lighter minerals which form the gangue. A very similar method is used in the separation of certain gems from gravel. On washing the gravel over a "greaser," diamonds are retained, while quartz particles and emeralds flow away in the stream of water. Another practical example of the influence of surface tension is perhaps shown in the effect of manganese in modifying the injurious action of sulphur on steel. Iron sulphide is said to form a skin round the crystalline grains of steel, thus weakening their cohesion; whereas manganese sulphide, instead of wetting the steel crystals, segregates into isolated, and therefore harmless particles.[1]

Surface Tension and Crystal Growth.—As has already been stated, surface tension involves, in the case of minute particles, so large an amount of free energy that precipitation is rendered difficult, and there is a universal tendency to reduce this free energy to a minimum, as shown, for example, in the coalescence of small drops to form large ones. For this reason, also, the presence of nuclei assists the process of precipitation. It is possible, however, that, in the case of the formation of clouds in the atmosphere, dust particles are not absolutely essential, since it has been pointed out that gaseous ions can act as nuclei if the supersaturation exceeds a certain value;[2] but such a process is exceptional, and requires a very high degree of supersaturation. The same principle of the free energy involved in surface tension assists in the explanation of the two degrees of supersaturation of liquids, which Ostwald has called the metastable and

[1] Manganese sulphide may, however, act thus on account of its earlier separation from fusion.

[2] Wilson, Phil. Trans. A., cxcii. 403; cxciii. 289, 1899.

labile states. Adopting Lehmann's view that the crystal form is the resultant of the forces of surface tension and molecular orientation, the conditions of equilibrium have been defined by Willard Gibbs.[1] He shows that the surface energy will not be the same on the different faces of a large crystal, and this would account for the rapid growth of certain faces at the expense of others. If we accept the view that surface tension is an important factor in crystal growth, it follows that crystallization will be most difficult to start in solutions in which the energy of the surface tension between the liquid and the possible solid is greatest. This view affords an explanation of the tendency of some solutions to become supersaturated, and the difficulty of producing supersaturation in others. The spontaneous development of crystalline nuclei in the labile state might then resemble the spontaneous condensation of water vapour upon nuclei consisting of ions; whereas in the metastable state only nuclei consisting of crystalline particles of the same or isomorphous species will induce crystallization. The phenomena are, however, still further complicated by internal molecular friction as has already been shown.

Supersolubility Curve.—Miers and Isaac have proposed the term "supersolubility curve" for the limit of the metastable region—that is to say, the region in which supersaturated solutions cannot crystallize spontaneously. Below this limit solutions pass into the labile state, in which spontaneous crystallization can take place. The supersolubility curve is approximately parallel to the solubility curve, its distance from which depends upon the respective solvent and solute.[2] It is not certain whether these conclusions

[1] Trans. Conn. Acad., iii. 494, 1874-78.
[2] Proc. Chem. Soc., xxii. 9, 60, 1906.

can be applied to fused salts, as Miers has worked so far only with aqueous solutions in which the influence of viscosity is not great.[1] Since in the metastable state crystalline nuclei are necessary to start crystallization, and in the labile state spontaneous crystallization ensues simultaneously at many points, it follows that the former will yield a few large crystals and the latter many small ones. From a kinetic standpoint, therefore, the difference between the metastable and labile states might be explained as the result of the increased solubility of the small crystals, which require a greater degree of supersaturation for their production.

Curie has stated that the total energy of a substance is made up of two parts, one of which is proportional to the volume and the other to the superficial area. On change of shape the volume energy remains constant, and the change of total energy is proportional to the change of surface. A crystal growing in a saturated solution has the tendency to build that form for which the total surface energy is a minimum, and each crystal face has a different capillary constant. Otherwise the stable form would be a sphere. The resulting form is that for which the total surface energy is a minimum, and it can be shown mathematically that a regular octahedron can only replace a cube when $\frac{A}{B}$ is greater than $\sqrt{3}$, A being the capillary constant for the cube face, and B that for the octahedral face.[2]

The growth of crystals in Nature will not often be in strict accordance with the theory of minimum surface energy, because this condition only follows when there is a state of perfect equilibrium between the crystal and its solution. Various disturbing

[1] *Vogt*, Tschermak. Min. u. Pet. Mitt., xxiv. 450, 1906.
[2] Bull. Soc. Min., viii. 145, 1885; *Ostwald*, Allg. Chem., i. 940.

factors, such as temperature variations, rapidity of growth, viscosity, and other causes, tend to disturb this equilibrium, and enable abnormal growths and skeleton crystals to form.

A considerable amount of research has been carried out with the object of showing the connection between surface tension and solubility.[1] From the analogy between the vapour pressure of fluids and the solution pressure of solid bodies, it would be expected that the solution pressure, and hence the solubility of a solid body, would be a function of the surface energy of the solid, and that its solubility would increase with the smallness of the particles of the solid body in contact with the solution. In a heterogeneous system consisting of a solution in contact with particles of various sizes, if the solution is saturated with respect to the smallest particles, it is supersaturated with respect to the largest; hence the latter will grow and the concentration of the solution will be diminished. The solution is then no longer saturated with respect to the small particles, and these are dissolved. This process will continue until the surface tension reaches a minimum, and only then will the system be in equilibrium. For this reason chemical precipitates become coarser in grain on standing,[2] and large crystals tend to grow at the expense of smaller ones. Ostwald has demonstrated these facts experimentally in the case of the red and yellow mercuric oxides. He also showed that the concentration of a saturated solution of barium sulphate can be increased as much as 20 per cent. by diminishing the size of the particles in contact with it.

This principle has been given as an explanation o

[1] *Curie, op. cit.*, p. 145; *Hulett*, Zeit. f. Phys. Chem., xxxvii. 385, 1901.

[2] *Ostwald*, Anal. Chem., 3 aufl., pp. 15, 23.

[3] Zeit. f. Phys. Chem., xxxiv. 495, 1900.

the differential weathering occasionally observed in the fluxion bands of obsidian and rhyolite, in which the texture varies in alternating bands.[1] In this case, however, it is not only a question of the relative saturation conditions of fine and coarse particles, but of the greater surface exposed by the fine particles to weathering agents. The above principle could only come into play if the products of decomposition remained *in situ* until equilibrium was attained.

The influence of surface tension on the growth of crystals in silicate magmas is shown by Vogelsang's observations upon the formation of globulites. These may be regarded as spherical drops of supersaturated solution, which ultimately coalesce into crystals. Their formation may be occasionally seen in slags, and in certain glassy rocks in which viscosity has increased too fast for the formation of perfect crystals.[2]

It is not certain, however, whether the globulite stage can be regarded as the universal starting-point of crystallization. Probably it is not so in the growth of crystals from solutions in the metastable state, in which crystalline nuclei form the centres of crystallization. While the metastable state persists small crystals could not be produced, for even if they happened to form they would be unstable, and would be absorbed into their larger companions. It is only when the solution reaches the labile state that a second generation of smaller individuals would be expected to be permanent.

Influence of Co-solutes on Crystalline Form.—Since the velocity of growth of the faces of a crystal is proportional to the capillary constant of these faces with respect to the mother liquor, any change in the

[1] *Iddings*, Seventh Annual Report U.S. Geol. Surv., p. 274; *Rutley*, Quart. Journ. Geol. Soc., lvi. 479, 1900.
[2] *Teall*, British Petrography, p. 194.

nature of the mother liquor will alter the capillary attraction[1] between it and the growing crystal.

Since, also, the capillary attraction of a liquid varies in contact with plates of different substances, so it may also vary with the physically different faces of crystals. This view has been also expressed by Retgers.[2] Thus, when urea is added to a solution of sodium chloride in process of crystallizing, the capillary attraction for the octahedral faces is increased, and these faces then grow in preference to those of the cube.

In Nature similar phenomena occur. Sodium chloride in presence of excess of calcium chloride crystallizes in octahedra in preference to the ordinary cubical form. Sodium chloride appears in the form of octahedra in the carnallite of Leopoldshall, and in the natron lakes of Egypt.[3] Potassium chloride exhibits similar behaviour. Calcium carbonate shows many anomalies when crystallized from complex solutions,[4] a fact which is of considerable interest in view of the many forms assumed by this mineral in Nature, and the rarity of the fundamental rhombohedron.[5] Lehmann gives other examples of similar phenomena.[6] All such occurrences are intelligible if it is considered that the surface energy of a crystal is a function of the nature of the solid and the liquid, and that the crystalline form is determined by the resultant of this and the crystallization force.

Becke, however, has arrived at an apparently different explanation. He maintains that the growing crystal tends to surround itself with faces of least

[1] *Curie*, Bull. de la Soc. Min. de France, viii. 145, 1885.
[2] Zeit. f. Phys. Chem., ix. 269, 1892.
[3] *Brauns*, Neues Jahrbuch, ii. 259, 1894.
[4] *Credner*, Journ. f. Prakt. Chem., cx. 292, 1870.
[5] *Vater*, Zeit. f. Kryst., 1893-99; see also Min. Mag., p. 39 December, 1903.
[6] Molekularphysik, i. 305.

solubility; and as the solution surface of a crystal varies in different media, the resulting crystalline form will vary also.[1] Since, however, solubility is a function of the surface energy, this may be only a different way of expressing the above-mentioned principle.

Colloidal Suspension and Surface Tension.— Turbid suspensions of clay and other finely divided matter are rapidly cleared by sea-salt, and even more quickly by the presence of certain other metallic salts.[2] This process, which is of some geological interest, has been variously explained. By some it has been attributed to chemical action, such as hydration or dehydration. More usually it is ascribed to physical causes depending upon an increase of surface tension owing to the presence of dissolved salts.[3] Thus, if the attraction of the particles for water exceeds the surface tension of the water, molecules of water will crowd towards the substance, and its particles being forced asunder, the substance will remain in suspension. If, however, the surface tension of the water exceeds the attraction of the solid particles for water, there will be a tendency for these particles to unite, and so diminish the surface energy by increasing the volume. This process increases the weight of the particles and allows them to settle.

It is probable that fine suspensions behave under the influence of electrolytic solutions in the same way as colloidal substances. The latter appear to behave as if the particles possessed an electrostatic charge. The solvent would then be likewise charged by induction, and the surface energy of the interface between the particles of colloid and solution would be modified by

[1] Tschermak. Min. u. Pet. Mitt., xi. 424, 1890.

[2] *Schulze*, Pogg. Ann., cxxix. 366, 1866; *Schloesing*, Comptes Rendus, lxx. 1345, 1870; *Spring*, Rec. Trav. Chim. Phys. Pays-Bas, pp. 222, 294, 1900.

[3] *Ladd*, Amer. Geol., xxii. 267, 1893.

the existence of an electric double layer.[1] Upon this assumption it would be easy to understand the influence of the addition of an electrolyte, the ions of which would annul the opposite charges of the electric double layer, and enable the particles to coagulate in obedience to the laws of surface tension. This explanation gives a reason for the observations of Linder and Picton, who found that the coagulative power of metallic salts depends upon their electric conductivity and valency—that is to say, upon their ionization and electric charge. Upon this view, finely divided matter in suspension in water will be precipitated with greater or less facility according to the presence of soluble salts, and thus the process of sedimentation in fresh and salt water may differ in a considerable degree.

Quincke has offered another explanation of the coagulative power of electrolytes, depending upon surface energy only. He assumes that the electrolytic solution, by spreading over the surface of the suspended particles, forms a new interface with the surrounding fluid; but this view does not seem to take into account the relation of coagulative power to the electric conductivity and valency of the dissolved salts.[2]

Colloids appear to play a part in many natural processes. Kahlenberg and Lincoln maintain that dilute solutions of silicates contain silica in the form of colloidal silicic acid. A dilute solution of an alkaline silicate, therefore, breaks up into alkaline hydrate and colloidal silica.[3] Possibly similar phenomena are exhibited by aluminates and ferrates, as suggested by Cameron,[4] and by natural silicates in general, as stated by Clarke.[5] In this way the peculiar properties of

[1] *Helmholtz*, Wied. Ann., vii. 337.
[2] Brit. Assoc. Rep., p. 60, 1901.
[3] Journ. Phys. Chem., ii. 88-90, 1898.
[4] Sixty-fourth Report U.S. Dep. Agric., p. 169, 1900.
[5] Journ. Amer. Chem. Soc., xx. 739-742, 1898.

colloidal solutions may enter largely into the explanation of many problems in chemical geology. The experiments of Cushman, for example, show that when crystalline rocks are ground up with water, there is at first a considerable increase in chemical action; hydrolysis takes place, alkaline silicates are removed in solution, and the particles of powdered rock become coated with a gelatinous film of aluminium silicate.[1] It follows from the above that colloidal substances are chemically inert, being but slightly, if at all, ionized. Such solutions differ also from solutions of electrolytes in a marked deficiency in molecular mobility and diffusive power.

Influence of Surface Tension on Chemical Action. —In the case of two liquids of unequal density the existence of surface tension at the interface would oppose their tendency to mix under the influence of osmotic pressure. Very little seems to be known upon this point, although Rayleigh has deduced mathematically an expression which requires equal density between two liquids in order that the surface tension at the interface may be zero.[2] The more abrupt the difference in density, the greater will be the energy due to surface tension. Poynting and Thomson suggest that, since chemical action between two liquids would cause a diminution in this potential energy, there would be a tendency for this chemical combination to take place. In the case of thin layers of liquid, therefore, there is present a factor which is absent in the case of liquids in bulk, and chemical reactions which do not take place under ordinary circumstances may then occur. We may, perhaps, partly ascribe to this cause the marked increase in chemical activity in the case of the action of solutions upon finely powdered

[1] Bulletin 92, U.S. Dep. Agric., p. 24 *et seq.*
[2] *Poynting* and *Thomson*, Properties of Matter, p. 180.

particles, as illustrated by the experiments of Cushman alluded to above. Upon the same principle may be explained the difference in the concentration of a solution between the surface and subjacent layers.[1] If the surface tension increases with greater concentration, salt will leave the surface layers; if it diminishes, the surface layers will be stronger in salt. Concentration, therefore, will vary in the successive layers until the osmotic pressure gradient becomes so great that the tendency to equalize the osmotic pressure balances the effects due to surface tension.

So far as investigations have yet been made, the surface tension of aqueous salt solutions in contact with air is greater than that of pure water. The exact relation is given by Dorsey[2] by the equation—

$$Tn = Tw + Rn,$$

where $Tn$ is the surface tension of a solution containing $n$ gramme equivalents of the salt per litre, and $Tw$ is the surface tension of pure water. The value of R has been determined for several salts, and for sodium chloride is 1·53.

The general result, which may be assumed to apply not only to aqueous solutions, but to liquid magmas, shows that the concentration in the surface layers will differ from that in the bulk, and, in contact with air, will, in the case of aqueous solutions, tend to cause a decrease in the concentration of the salt in the surface layers so long as there is no loss of solvent by evaporation.

Capillarity Phenomena.—The height to which liquids will rise in capillary tubes may be used to measure their surface tension. Thus, if T is the surface tension in dynes per square centimetre, $r$ the

[1] *Ramsden*, Proc. Roy. Soc., lxxii. 156.
[2] *Dorsey*, Phil. Mag., xliv. 369, 1897.

radius of the tube, D the density of the liquid, and $d$ the density of the gas in contact with the liquid, then $T = \frac{1}{2} ghr(D - d)$.

In capillary tubes the equilibrium at the line of contact between air, solid and liquid, is the resultant of three surface tensions, as already explained. Since the surface tension of most salt solutions in contact with air is found to be greater than that of pure water, the surface tension between the solid and the liquid wetted by it must be less in order that equilibrium may be possible in accordance with the condition that $T_2 = T_1 - T_3$.[1]

Hence the layer of liquid in contact with the solid will become richer in salt than the bulk of the solution.[2] Therefore, if salt solution is filtered through capillary tubes, salt tends to collect along the walls, and the faster moving central parts will have their concentration diminished. In this way Thomson and Monckman filtered potassium permanganate from its solution by passage through finely divided silica.[3] Similar phenomena are observed when dilute coloured salt solutions are absorbed by blotting-paper. There are many interesting illustrations of this process in Nature, of which a familiar example is furnished by "banded flints," the zones of absorption becoming gradually colourless by loss of salt. The penetration of dilute solutions into capillary fissures and cleavage planes of rocks and minerals is a universal occurrence in the earth's crust. In this connection, the researches of Skey[4] and of Kohler,[5] confirmed later by Weed,[6] are significant. These observers have proved experi-

[1] See *ante*, p. 58.
[2] *J. J. Thomson*, Application of Dynamics to Physics and Chemistry.
[3] *Whetham*, Theory of Solutions, p. 97.
[4] Trans. New Zealand Inst., ii. 151, 1869; iv. 332, 1871; vii. 387, 1874.
[5] Zeit. f. Prakt. Geol., p. 49, 1903.
[6] Eng. and Min. Journ., February 23, 1905.

mentally that clays and finely divided silica possess the property of absorbing metals from their solutions. The action seems to be closely related to the capillarity phenomena described above. The importance of capillary transmission has also been illustrated by King, who has determined experimentally the rate at which water is capable of being raised in porous rocks in opposition to gravity,[1] a phenomenon possessing considerable practical importance in connection with irrigation.

The deposition of mineral matter under the influence of surface tension may, therefore, explain many occurrences in Nature. The importance of capillary action in connection with percolation has been investigated by Ladd.[2] Becker, also, has pointed out the influence of this factor in connection with ore deposits. When mineral solutions are absorbed by the wall rock, the molecular actions called into play by capillary action have an influence upon the concentration of the mineral matter.[3] Every kind of osmotic action, as observed by Tait, is complicated by molecular actions between the septum and the fluid which percolates through it.[4] Interesting examples of this process are cited by Way.[5]

Adsorption Phenomena.—Closely related to capillary phenomena and to surface energy is the property known as adsorption. This term was suggested by E. du Bois-Raymond to denote the power possessed by many solids, especially when in a porous or powdery state, of condensing gases upon their surfaces. The phenomena have been studied by several observers.

[1] *King*, Nineteenth Annual Report U.S. Geol. Surv., ii. 85, 1899.
[2] Amer. Geol., xxii. 267, 1898.
[3] *Becker*, Min. Res. U.S., p. 139 *et seq.*, 1902.
[4] Properties of Matter, p. 275, 1890.
[5] Journ. Roy. Agric. Soc., xi. 316, 1850; also *Sullivan*, Bull. U.S. Geol. Surv., No. 312.

Thomson has suggested that the conditions of equilibrium in such cases are determined by the question whether the final state leads to a decrease or increase of surface tension. In the former case chemical action will be accelerated, in the latter case it will be retarded.[1] It is probable that in the pneumatolytic processes which take place in rocks the nature of the mineral surfaces has a selective action upon condensation and the formation of minerals. The tenacity with which films of air adhere to the surfaces of glass vessels is well known, but it is still a matter of uncertainty whether such phenomena are due to chemical action, to occlusion, or to the formation of solid solutions.

Similar phenomena are observed in the case of liquids, and have been held to explain the formation of coloured crystals by contact with organic colouring matters.[2] The phenomena of adsorption in liquids have been studied by Freundlich,[3] who concludes that in general those substances are adsorbed which lower the surface tension between the solid and the liquid. Adsorption is most marked in the case of solvents which have a high value for the surface tension between solid and liquid, the general result being towards a minimum surface tension. The influence of solids upon the concentration of the surface layer of liquids in contact with them is important from a geological standpoint. This contact film appears to be the active agent in the transfer between the free solution and the solid. The migration of dissolved material seems to be to some extent checked by the molecular attraction of the solid.[4]

[1] *Van 't Hoff*, Studies in Chemical Dynamics, p. 43, 1896; *Thomson*, Application of Dynamics to Physics and Chemistry, p. 206, 1888.

[2] Zeit. f. Phys. Chem., viii. 543; xiv. 157; xv. 56, 1894.

[3] *Ibid.*, pp. 385-470, 1906.

[4] *Cameron*, "Application of the Theory of Solution to the Study of Soils," Sixty-fourth Report U.S. Dep. Agric., p. 142, 1900.

The presence of a solid may, therefore, influence the kind of reaction that takes place in a solution by enabling an adherent film to become supersaturated in advance of the remainder of the solution. Thus may be explained the tendency of mineral particles to grow in preference to the formation of new individuals, the solid exerting a selective power by abstracting like molecules from the solution and rejecting unlike molecules.[1] This is possibly the reason for the numerous cases of secondary growth commonly observed in such minerals as quartz and felspar in rocks. It also explains why in many cases of rock cementation the cement resembles the solid originally present, quartzose sandstone being often cemented by silica, and felspathic sandstone by felspar. The presence of the solid exerts an influence upon the grouping of the molecules and ions present in the solution, and causes the separation of similar solid material even from comparatively dilute solutions. Excellent examples of such secondary enlargement of minerals in sedimentary rocks, owing to the action of aqueous solutions, are furnished by many sandstones, as Sorby[2] long ago pointed out. A remarkable case in the Keeweenawan sandstone of Lake Superior has been described by Van Hise.[3] In this case grains of orthoclase and plagioclase are enlarged by secondary deposition of the material in optical continuity with the original crystals even to the extension of the twinning lamellæ. Similar enlargements of hornblende crystals in the volcanic tuffs of Kekakabic Lake, in the north-east of Minnesota, have been noticed by the same observer,[4] who has also given

[1] *Ostwald*, Grundlinien der Anorganischen Chemie, pp. 387-389, 1900.
[2] *Sorby*, Proc. Geol. Soc., p. 62, 1880; *Judd*, Quart. Journ. Geol. Soc., xlv. 178, 1889.
[3] Bull. U.S. Geol. Surv., viii. 44-47, part 2, 1884.
[4] *Van Hise*, Amer. Journ. Sci., xxx. 231-235, 1885; xxxiii. 385, 1887.

numerous other illustrations of the influence of pre-existing crystals in controlling chemical reactions in dilute solutions percolating through rocks.[1]

It appears as if a crystallization force exists which is capable of acting across space, and is selective in character, a growing crystal being capable of bringing together molecules from a distance.

The very numerous phenomena which in geology are grouped under the terms "segregations" and "concretions" are thus brought together and explained by the principle of adsorption.

[1] *Van Hise*, Treatise on Metamorphism, p. 644 *et seq.*, 1905. See also *Bödlender*. Neues Jahrbuch f. Min., bd. xii. : *Doelter*, Physikalisch-Chemische Mineralogie, pp. 82, 83.

# V

## VAPOUR PRESSURE AS A FACTOR IN EQUILIBRIUM CONDITIONS

Experiments have shown that many solids possess a appreciable vapour pressure at moderate temperature and by the aid of the electric furnace the boiling point of certain metals have been ascertained.[1] Halloc showed the existence of vapour pressure in soli sulphur;[2] and Osann has described the volatilizatio of blast-furnace slag when heated to a temperature c about 2000° C.[3]

At ordinary temperatures the vapour pressure c most solids is small. This fact has greatly simplifie the study of transition points, and the conditions c equilibrium in systems composed of solid and liqui phases. The error involved in neglecting the vapou phase under such conditions may be assumed to b immaterial.[4] At the high temperatures prevailing i the deeper parts of the earth's crust, however, vapou pressures cannot be ignored.

The condition that a substance shall sublime—tha is, vaporize without melting—may be inferred fro a study of the pressure-temperature diagram. If th melting point is raised by pressure, the fusion curv

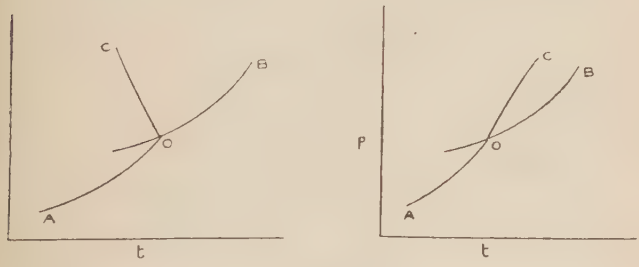
[1] *Moissan*, Comptes Rendus, cxli. 977, 1905. Partial vaporizatio at temperatures below the boiling point has also been proved (s Berichte, vol. xxxvi.).

[2] Amer. Journ. Sci., xxxvii. 405, 1889.

[3] Stahl und Eisen, p. 870, August, 1903.

[4] *Van't Hoff*, Studies in Chemical Dynamics, p. 163.

OC slopes away from the pressure axis, as in Fig. 8. f the melting point is lowered by pressure, the fusion urve slopes towards the pressure axis, as in Fig. 7. The point O is a triple point, where the fusion curve OC, the vaporization curve OB, and the sublimation urve AO meet. Thus at any temperature below the riple point along the curve AO the substance will ublime so long as the sublimation pressure is greater han the pressure it supports. Moissan found that on eating lime in the electric furnace it was vaporized nd crystallized in cubes on the cooler parts.[1] Prac- ically nothing is known of the actual pressure of the




FIGS. 7, 8.—PRESSURE-TEMPERATURE DIAGRAMS OF A SINGLE COMPONENT SYSTEM.

apour of solids, but it is theoretically possible, and lso probable, that vaporization takes place in plutonic egions notwithstanding the pressure. Arrhenius, ndeed, assumes that all matter would be above its ritical temperature, and therefore in a gaseous state, n the deep-seated parts of the earth.[2]

DISSOCIATION PHENOMENA.—It will be convenient ow to consider the conditions of equilibrium in ystems of two components in presence of a vapour hase, as illustrated, for example, by the action of heat

[1] Comptes Rendus, cxxxiv. 136, 1902.
[2] Zur Phys. des Vulkanismus, pp. 395-419, 1900.

upon calcium carbonate, and upon various mineral
Taking first the case of calcium carbonate, the di
sociation of this substance by heat is represented b
the reversible reaction shown by the equation—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The conditions of equilibrium are indicated by th
accompanying diagram (Fig. 9), representing the di
sociation pressure curve of calcium carbonate
different temperatures and pressures. The curve thu
obtained represents the equilibrium condition
$CaCO_3$, CaO, and $CO_2$. The system is univariant-
that is to say, for every temperature there is a defini

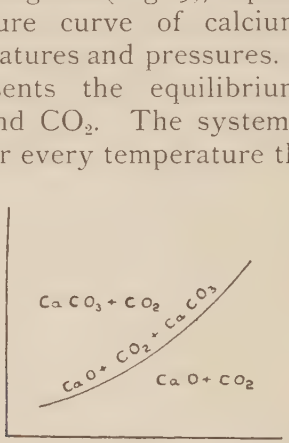



Fig. 9.—Dissociation Curve of Calcium Carbonate.

dissociation pressure of calcium carbonate. In th
field below the curve only two phases—CaO an
$CO_2$—can exist together, and in the field above th
curve only $CaCO_3$ and $CO_2$ can coexist.

The dissociation pressure of calcium carbonate w
determined by Debray,[1] and later, with more accurac
by Le Chatelier.[2] At 812° C. this pressure is equ
to one atmosphere. At this temperature, therefor
calcium carbonate can be completely dissociated
presence of carbon dioxide at atmospheric pressur
By increasing the pressure until the partial pressure
the carbon dioxide exceeds the dissociation pressu

[1] Comptes Rendus, lxiv. 603, 1867. [2] *Ibid.*, cii. 1243, 1883.

of calcium carbonate the latter does not dissociate, whatever may be the temperature to which it is exposed. It is important to note that this result depends upon the condition that the products of the reaction are not removed from the sphere of action. If the carbon dioxide is removed as fast as it is formed, dissociation can proceed at a far lower temperature, since the dissociation equilibrium of the carbonate depends not upon the pressure to which it is subjected, but upon the partial pressure of the carbon dioxide in contact with it.

These facts have a bearing upon the occurrence of crystallized calcium carbonate in Nature. Hutton first pointed out in 1798 that the calcium carbonate in the limekiln only bears the pressure of the atmosphere, whereas in plutonic regions an enormous pressure exists, and may hinder its decomposition and allow it to fuse and crystallize.[1] Hall verified this conclusion experimentally in 1804.[2] It was not until 1837, however, that Aimé[3] called attention to the fact that "when a body is decomposed by heat it is not the pressure of any gas or vapour, chosen at random, that can stop its decomposition; it is the gas which arises from the decomposition which alone can act." This important principle, which follows at once from the application of the phase rule to dissociation phenomena, is sometimes lost sight of in geological reasoning. It is not pressure *qua* pressure which must be considered, but the partial pressure due to carbon dioxide.

In considering whether it is possible for calcite to occur as a primary constituent of igneous rocks, we have to discuss the problem in the light of the above fundamental principle. Hall's experiments, alluded to

[1] Trans. Roy. Soc. Edinb., iv. 7, 1798. [2] *Ibid.*, v. 43, 1805.
[3] See *Duhem*, Journ. Phys. Chem., iii. 364, 1899.

above, seemed to suggest that marble may be th result of the fusion of chalk at high pressure. Th fusibility of calcium carbonate has been examined i detail by Becker, who investigated the relation of i fusion point to its dissociation temperature.[1] Th latter, under moderate pressures, is below the fusio point. Le Chatelier was the first to show that chal can be fused at 1000° C. if the partial pressure of th carbon dioxide upon it exceeds 1,000 kilogrammes pe square centimetre.[2] He concluded that, under sufficient pressure of carbon dioxide, calcite ca separate from a molten magma. Bourgeois, indee claimed to have produced hexagonal crystals of calciu carbonate from a fused mass of that substance in th presence of the chlorides of sodium and potassium.[3]

A primary origin has been claimed for calci occurring in certain nepheline syenites in Souther India,[4] Ontario,[5] and Alnö.[6] A similar origin has bee suggested as a possibility for the calcite in the so-calle calcite granite of Sudbury,[7] New Hampshire,[8] an Guomalo in Sweden.[9] The phenomena accompanyin certain limestone masses in Burmah[10] and in Ceylon have been held to point to an origin from a conditio "akin to fusion." Very interesting in this connectio is the description by Emerson of calcite, and als ankerite, forming spherulites in the glass of th diabase-aplite of Holyoke. Here a broad zone

[1] Tschermak. Min. u. Pet. Mitt., vii. 122-145, 1886.
[2] Comptes Rendus, cxv. 817, 1892.
[3] Zeit. f. Kryst., xx. 276.
[4] *Holland*, Mem. Geol. Surv. India, xxx. 197, 1901.
[5] *Adams*, Amer. Journ. Sci., xlviii. 14, 1894.
[6] *Törnebohm*, Geol. Fören. Stockholm, Förh. xvii. 100, 214, 1895.
[7] *Walker*, Quart. Journ. Geol. Soc., liii. 55, 1897.
[8] *Hawes*, Report on the Geology of Vermont, iii. 190-220 ; see al *Chrustschoff*, Mém. Acad. Imp. des Sci. de St. Petersb., Ser. 42, No. vii., 1894.
[9] *Törnebohm, loc. cit.*
[10] *Holland, op. cit.*
[11] Quart. Journ. Geol. Soc., lviii. 399, 1902.

glass is seen sometimes to surround a calcite crystal; in other cases, feathery calcite or ankerite spherulites have separated in the midst of fresh, unaltered glass. The conclusion seems to be clear that these separated from a fused magma in which calcite existed in solution.[1]

The problem is complicated by the frequency with which calcite occurs as a product of alteration in igneous rocks; and although physical considerations present no obstacle to the formation of calcite from igneous fusion under certain conditions, chemical considerations seem to preclude such an origin in the majority of silicate magmas.

Another point of interest in connection with the stability of calcite is presented by the phenomena of contact metamorphism in the crystalline limestones. A distinction is here necessary between crystalline limestones altered by contact metamorphism and secondary limestones produced by the action of carbon dioxide upon silicate rocks. To the latter belong certain calciphyres and cipollinos in Southern India, Ceylon, and Burmah, the main source of the calcite being the plagioclase of the parent rock, thus: $CaO.Al_2O_3(SiO_2)_2 + CO_2 = CaCO_3 + 2SiO_2 + Al_2O_3$.[2]

Teall has pointed out that the Durness dolomite in proximity to the plutonic complex of Cnoc-na-Sroine occasionally shows varieties of marble, composed of calcite and brucite, the latter mineral being pseudomorphous after periclase.[3] This rock resembles the predazzite of the Tyrol, and appears to show that magnesium carbonate parted with its carbonic acid more readily than the calcium carbonate. In such cases there is evidence of the loss of carbonic acid on

[1] *Emerson*, Bull. Geol. Soc. America, xvi. 105-120, 1905.
[2] *Fermor*, "Petrology of the Chindwara," Rec. Geol. Surv. India xxiii. 216, 1906.
[3] *Teall*, Rep. Brit. Assoc. Southport, Section C, p. 660, 1903.

a large scale, since silicates, such as forsterite, tremolite, and diopside, are extensively developed in the contact zone. Dissociation phenomena are here, however, complicated by chemical reactions, and we no longer can apply the simple rules of equilibrium on the vapour pressure curve.

Hydrated Minerals. — There is no satisfactory explanation of the retention of the so-called water of crystallization. Still less is known of the precise definition of water of constitution. Those crystalline hydrates which are liable to effloresce have been regarded as consisting of a space lattice of water, probably in the solid phase, in the meshes of which the other constituents are arranged; but in other cases, as, for example, many of the zeolites, it seems more probable that the space lattice consists of the mineral substance, and that the water is held in the meshes. In its narrower sense, the term "water of constitution" is restricted to compounds containing the hydroxyl group, but it is not always easy to determine whether a hydrated compound is a hydrate or a hydroxide. When hydration and dehydration can take place reversibly, the water of crystallization may be assumed to be present in the molecular state. In such cases the equilibrium conditions resemble those of a liquid in contact with its vapour.

A distinction has sometimes been drawn between true hydrates and hydroxides by means of the temperature of the transition point at which the hydrated compound loses its combined water. Thus, one of the hydrates of magnesium sulphate, $MgSO_4.7H_2O$, loses six molecules of water at 132° C., while the last molecule is only driven off completely at 210° C. Graham, who noticed that some part of the water of crystallization is retained at a higher temperature than the rest, has proposed to call this firmly-held water "water

of hal-hydration." Erlenmeyer considered this to be water of constitution.[1]

Coblentz[2] has recently proposed to determine the manner in which water is held in crystals by the examination of the infra-red absorption spectra. Water exhibits well-marked bands at various wave lengths in this portion of its absorption spectrum. These same bands are well shown by certain hydrated minerals, such as selenite, opal, heulandite, stilbite, natrolite, and scolecite. Minerals containing the hydroxyl group show a different absorption spectrum, typically seen in the case of manganite, göthite, bauxite, diaspore, and other substances.

We may regard the transition point of a hydrate as the temperature at which the vapour tension of the hydrate first exceeds the partial pressure of the water vapour in contact with it. When a hydrate has a high transition temperature, it may mean either that its vapour pressure is small at low temperatures, or that its transformation proceeds so slowly at low temperatures as to escape notice.[3]

The vapour pressure of a salt is related to its solubility by the law that at a given temperature the less stable form has the higher vapour pressure, and is the more soluble. Thus, when a solvent acts upon a substance which is present in two phases, the less stable phase is dissolved, and the solution becomes supersaturated with respect to the more stable phase, which is, therefore, deposited. At the transition point the two phases have the same vapour pressure, and the solubilities are then equal.

It is for this reason that pressure may invert the

[1] *Fock*, Chemical Crystallography, translated by *Pope*, pp. 30, 31.

[2] Phys. Rev., xxiii. 125, 1906.

[3] The vapour pressure of hydrates can be conveniently measured by the Brenier-Frowein tensimeter, described in Zeit. f. Phys. Chem., 5, 1887; xvii. 52, 1895. See also *Findlay*, The Phase Rule, p. 88.

order of solubility of two substances. Thus, a ordinary pressures calcium carbonate is more solubl than magnesium carbonate, but at higher pressure magnesium carbonate is the more soluble salt. Henc at an intermediate pressure the solubilities becom equal, and the double salt dolomite may be formed.[1]

The solubility curve may thus be used to determin the vapour pressure of a substance. Hulett and Alle deduced the transition point of gypsum by findin where its solubility curve cuts the vapour pressur curve of water. At this point (107° C.) the vapou pressure of gypsum is equal to that of water at th temperature.[2]

Dissociation of Hydrates.—The conditions unde which dehydration or the converse takes place are i every way similar to the dissociation phenomena calcium carbonate described above A system of th kind consists of two components, anhydrous salt an water, in three phases—namely, hydrated salt, an hydrous salt (or a lower hydrate), and vapour. Such system is univariant. For every temperature there wi be a definite dissociation pressure. When this is les than the vapour pressure of the system, more hydra will form; when greater, the hydrate loses water, an may ultimately become completely dehydrated. Th is exactly analogous to the condition of equilibriu between a liquid and its vapour.

The time necessary for hydration and dehydratio depends, among other things, upon the differen between the vapour pressure of the hydrate and th partial pressure of the aqueous vapour in the surroun ing medium.

Many natural hydrates, however, appear to have n definite chemical composition, and no transition poi

[1] *Skeats*, Quart. Journ. Geol. Soc., lxi. 135, 1905.
[2] Journ. Amer. Chem. Soc., xxiv. 667, 1902.

This Ramsay found to be the case with some amorphous forms of ferric and aluminium hydrates.[1] Such substances, in their amorphous form, may be regarded as solid solutions.

Hydrates may be divided, therefore, into two classes: (1) Those with a definite transition point; (2) those with no definite transition point.

Gypsum and Anhydrite.—Many natural hydrates belong to the first type—that is, they have a definite vapour pressure—and at a certain fixed temperature, depending upon the pressure of the aqueous vapour in the surrounding atmosphere, or in the solution in contact with them, they lose water and pass into lower hydrated forms or into anhydrous mineral. Of this class calcium sulphate forms an interesting example on account of its widespread geological occurrence, both in the form of the hydrous salt, gypsum, and the anhydrous form anhydrite.

The occurrence of anhydrite in Nature has long been a subject of controversy in chemical geology. Many researches have from time to time been made to determine the conditions under which the anhydrous salt could be deposited in water. The history of these researches illustrates the peculiar difficulties often involved in the experimental investigation of such phenomena. As early as 1849 Usiglio evaporated sea-water on a large scale, hoping to reproduce in this way the precise order of separation of salts as seen in the Stassfurt deposits.[2] He failed, however, to obtain anhydrite, and the order of separation did not agree with that of the Stassfurt salts. Subsequent researches by Van 't Hoff and others have shown the reason for his failure. He did not allow time for the solution to arrive at the equilibrium stages corresponding to the

[1] Journ. Chem. Soc., xxxii. 395, 1877.
[2] Ann. de Chim. et de Phys., xxvii. 92, 172, 1849.

varying concentrations as evaporation proceeded. A the present time we are only concerned with on portion of the problem which Usiglio attempted t solve — namely, why calcium sulphate should b deposited from solutions sometimes as anhydrite an at other times as gypsum. The key to the problem, a can be inferred from what has gone before, lies in th determination of the vapour pressure of the hydrat as compared with that of the solution at differen temperatures.

Gypsum can be readily and completely dehydrate by heating it in dry air.[1] Between 98° C. and 130° C the loss of water is continuous and complete, bu natural anhydrite is not produced by this means. I its place is obtained a form of anhydrous calciu sulphate which is very soluble in water, and whic absorbs moisture from the air; whereas natura anhydrite is a comparatively stable mineral, onl becoming hydrated after very prolonged contact wit water. Similarly, if gypsum is heated in contact wit water, the dilatometer experiments of Van 't Hoff an Armstrong show a marked increase of volume at a temperature of about 107° C.,[2] there being produced a this temperature a lower hydrate, known as plaster o Paris or the half-hydrate $CaSO_4.\frac{1}{2}H_2O$. As state above, also, Hulett and Allen found that at this sam temperature, 107° C., the solubility curve of gypsu cuts the vapour pressure curve of pure water. A this temperature, therefore, the vapour pressure of th system gypsum—half-hydrate is equal to the vapou pressure of water. At a higher temperature th vapour pressure of the hydrate increases mor rapidly than that of water, and at 132° C. the half hydrate loses water, and passes into the same soluble

[1] Journ. Soc. Chem. Ind., xxvi. 729, 1907.
[2] Sitz. d. K. Akad. d. Wiss., p. 570, 1900.

form of anhydrite as is got by heating gypsum in dry air. At a still higher temperature—namely, 525° C.—this soluble anhydrite passes into the insoluble form of natural anhydrite. Calcium sulphate in solution in water, therefore, cannot be deposited as anhydrite unless the vapour pressure of the gypsum exceeds that of the solution in contact with it. To secure this result, either the vapour pressure of the gypsum must be increased by raising the temperature or the vapour pressure of the solution must be reduced, since at all temperatures below 107° C. the hydrate has a lower vapour pressure than pure water. In the natural formation of anhydrite, however, we are not dealing with a simple solution, but with a complex solution of soluble salts. We have to consider, therefore, the influence of co-solutes.

The presence of any substance in solution which lowers the vapour tension of water will lower the inversion temperature of gypsum. It is to the influence of co-solutes, therefore, that the formation of anhydrite from salt solutions is due. This tendency to dehydration in salt solutions is well illustrated in the evaporation of a solution of magnesium sulphate in presence of magnesium chloride, when, instead of bitter salt, $MgSO_4.7H_2O$, kieserite, $MgSO_4.H_2O$, is formed.[1] Similarly, from pure sodium sulphate solution evaporated at ordinary temperature glauber salt, $Na_2SO_4.10H_2O$, is deposited, but in presence of sodium chloride thenardite, $Na_2SO_4$ is formed.[2] So also, instead of gypsum, $CaSO_4.2H_2O$, from a solution containing calcium sulphate in presence of NaCl or KCl, anhydrite is deposited at a temperature of 30° C.[3] Even solid gypsum, at a somewhat higher temperature, can be

[1] Berichte, xiv. 2131, 1881.
[2] *Retgers*, Neues Jahrbuch f. Min., i. 276, 1891.
[3] *Brauns*, Neues Jahrbuch, ii. 259, 1894.

changed into anhydrite by a concentrated solution o sodium chloride.[1] In this case the concentration of th salt solution appears to be important. A dilute solu tion of NaCl has been found to accelerate hydration but at concentrations greater than 6 per cent. it retard the process.[2] These facts are of interest as pointing to the possibility of the dehydration of minerals i rocks, in contact with salt solutions, at a temperatur considerably below their normal inversion point.

The physical explanation of this action of co-solute is to be found in the fact that their presence in solu tion, supposing there is no common ion, increases th osmotic pressure and lowers the vapour pressure o the solution, thus acting in the same direction as a ris in temperature by facilitating the production of mor of the vapour phase at the expense of the hydrate salt. Thus the vapour tension of a concentrated solu tion of sea-salt at 25° C. is less than 17·2 millimetres which is the vapour tension of gypsum at that tempera ture, so anhydrite is deposited instead of gypsum The influence of co-solutes explains other occurrence in Nature where a mineral has been deposited from solution in a lower state of hydration than is pro duced at ordinary temperatures in the laboratory For example, the ordinary sodium carbonate $Na_2CO_3.10H_2O$, rarely occurs as a natural product although it is stable at temperatures below 37° C. Th forms which occur more commonly as natural product are thermonatrite, $Na_2CO_3.H_2O$, which can be prepare artificially at temperatures above 37° C.; or trona $Na_2CO_3.NaHCO_3.2H_2O$, and the double salt gay lussite, $Na_2CO_3.CaCO_3.5H_2O$.

[1] *Spring* and *Lucion*, Zeit. f. Anorg. Chem., ii. 195-220, 1892.

[2] *Le Chatelier*, Ann. d. Min., 1892; Thon Industrie Zeitung, p. 103 1899. See also *Poynting*, Phil. Mag., xlii. 289, 1896. He explains th lowering of vapour tension in such cases by association of the dis solved molecules with those of the solvent.

The influence of a saturated solution of sodium chloride upon the production of anhydrite was first recognized in 1866 by Hoppe-Seyler,[1] but both he and Rose concluded that a high temperature, between 125° C. and 130° C., was necessary for the transformation. It was Posepný who showed that in the presence of much magnesium and calcium chloride anhydrite could be deposited at ordinary temperatures.

The problem, however, cannot yet be considered as definitely settled, since in no laboratory experiments has natural anhydrite been produced at a low temperature, but only the soluble form, which is not found in Nature. Vater,[2] and later Davis,[3] have given a reason for this. Gypsum, like many other hydrated salts of bivalent metals, is dimorphous, existing in both the monoclinic and orthorhombic forms. Two distinct series of salts may, therefore, exist. In the laboratory the orthorhombic series is invariably produced. In Nature, where the time factor is large, the monoclinic series is formed. Whenever gypsum is dehydrated in the laboratory, it first passes into the orthorhombic modification.

Hydrated Iron Oxides.—The circumstances which control the hydration and dehydration of iron oxides have a special interest in chemical geology. Van Bemmelen has shown that the red-brown body obtained by precipitating ferric salts with an alkali, and commonly known as hydrated ferric oxide, is a colloid.[4] As such it has no definite composition, and is capable of indefinite modification, but always in the direction of getting into equilibrium with the tension of the water vapour in contact with it. He considers that the compound described as $Fe_2O_3.H_2O$

[1] Pogg. Ann., pp. 127, 161, 1886.
[2] Sitz. d. K. Akad. d. Wiss., p. 270, 1900.
[3] Journ. Soc. Chem. Ind., xxvi. 727 *et seq.*, 1907.
[4] Rec. des Trav. Chim. des Pays-Bas, vii. 36-118, 1888.

is a chance limit of water content, depending upon the temperature and moisture of the surrounding atmosphere. The yellow colloidal hydrate is, in his opinion, not a specifically different modification of the red-brown variety, but a more stable and condensed condition. Tommasi had previously classified the artificially precipitated iron oxides into two groups: (1) the red hydrates, obtained by precipitating ferric salts with an alkali; (2) the yellow hydrates, obtained by oxidizing ferrous oxide or carbonate. He states that the former is more readily dehydrated than the latter, and passes ultimately into the anhydrous form, whereas the yellow hydrates cannot be completely dehydrated by heat.[1] Van Bemmelen and Klobbie, however, maintain that the red colloid passes gradually at ordinary temperatures into a more stable, less hydrated, and denser form, but without any end product being reached or definite hydration determined.[2] Ruff has endeavoured to illustrate experimentally the formation of iron hydrates in nature.[3] He shows that, although the water content of freshly precipitated colloid hydrates depends upon the vapour tension of the surrounding air, and has no fixed proportions, yet old material which has been once dehydrated behaves differently. Some of his experiments extended over periods ranging from six to fifteen years, and demonstrated that dehydration proceeds very slowly at ordinary temperatures and is never complete. At temperatures between 50° C. and 60° C. the change proceeds much faster, a few days producing the same result as years at ordinary temperatures. He also confirmed the greater reluctance of the yellow colloid to part with its water of hydration.

[1] Berichte, xii. 1929, 2334, 1879.
[2] Journ. f. Prakt. Chem., xlvi. 497, 1892.
[3] Berichte, xxxiv. 3417, 1901.

On the whole, it seems probable that the hydrates obtained by the oxidation of ferrous hydrate or carbonate differ in their properties from those got by direct hydration of ferric salts.[1] If it is assumed that natural hydrates possess different degrees of energy of transformation, and that hydration and dehydration are reversible processes, depending upon an equilibrium with the vapour tension of the air to which they are exposed, the many forms assumed in Nature by these compounds may possibly be explained. The chief point to bear in mind with regard to the amorphous hydrates is that they do not possess a definite composition, and have no sharp transition point.

Zeolites.—The zeolites form a typical example of crystalline hydrated compounds which possess no sharp transition point, and behave as solid solutions, in which the water appears to exist in a state of mixture rather than of chemical combination. Zeolites may, in some cases, be dehydrated without loss of crystalline form, and readily reabsorb moisture, regaining their original transparency. They possess a vapour tension which varies continually with the concentration of the water contained in them.[2] They form, therefore, univariant systems, consisting of one component and two phases, solid and vapour. This property is well illustrated by analcime, studied by Friedel.[3] Suppose that this mineral is in equilibrium with water vapour at a tension P. If some of this vapour is removed, the mineral undergoes partial dehydration, but the tension of the vapour only rises to a value P′, which is less than P, showing that we are here dealing, not with a definite hydrate with an invariable dissociation tension, but with a

[1] *Muck*, Zeit. f. Chem., xli. 1868.

[2] *Chapuis*, Wied. Ann., xii. 161, 1881 ; *Joulin*, Ann. d. Chim. et de Phys., xxii. 398, 1881 ; *Kayser*, Wied. Ann., xii. 526, 1881.

[3] *Friedel*, Bull. de la Soc. de Min., xix. 363, 1896 ; xxi. 5, 1898.

solid solution, in which water is merely absorbed int the meshwork of the crystalline structure.

Tammann has extended these observations to a larg number of hydrated minerals.[1] This behaviour like wise characterizes some of the chlorites, as describe by Heddle.[2] Thus saponite readily parts with som of its water on warming it to a moderate temperatur and regains it on cooling in a moist atmosphere. Th explains the darkening of chloritic patches in drie igneous rocks when they are breathed upon. Th vigorous hygroscopic character of dehydrated zeolite is turned to practical account for their recognition i rock slices.

More recently the subject of the constitution zeolites has been studied by Zambonini and by Ferr The former, experimenting upon the dehydration heulandite and thomsonite, concludes that only portion of the water is expelled in a vacuum ove sulphuric acid at ordinary temperatures, and it is onl this part of the process which is reversible. Th water expelled at high temperatures is not reabsorbed Similarly Ferro found that heulandite contains 3 mol cules of water more intimately combined than the res which latter may be described as hygroscopic water Zambonini, therefore, considers that the zeolites ar not hydrates. He regards them rather as analogou to the hydrogels studied by Van Bemmelen, their stat of hydration depending upon the temperature an concentration of the vapour phase, while prolonge heating renders them incapable of reabsorbing wate Sommerfeldt, from a consideration of the heat effe accompanying the hydration of analcime, has arrive

[1] Wied. Ann., lxxiii. 16, 1897; Zeit. f. Phys. Chem., xxvii. 32 1898.
[2] Trans. Roy. Soc. Edinb., xxix. 55, 1880.
[3] Mem. Roy. Acad. Lincei, xiv. 140, 1905.
[4] *Ibid.*, v. 344, 1905.

at the conclusion that the phenomena exhibited by zeolites are connected with adsorption.[1]

A question of interest from a petrographical point of view is whether certain zeolites in igneous rocks are of primary origin. The analcime rocks are a conspicuous example. Monchiquites and analcime basalts have been described from many localities,[2] and a primary origin has been claimed for the analcime which they contain. While in some cases the analcime is probably secondary, there are reasons for concluding that it may be of primary origin in others. This view is supported by many considerations. Thus, the zeolites appear to require an elevated temperature for their formation in certain cases. This is exemplified by their occurrence in the thermal springs of Plombières, as described by Daubrée,[3] Both Geikie and Harker consider that the zeolites in amygdaloidal rocks were generally deposited while the rocks were still hot.[4] It is also well known that water and certain fused salts are miscible in all proportions. Barus has shown that molten glass can be so impregnated with water that, on cooling, an aqueous glass is formed,[5] in which the water is retained.[6] That the water of hydration of zeolites depends also upon the pressure is also established. At ordinary atmospheric pressures analcime is completely dehydrated at temperatures above 400° C.,[7] and under great pressures it is possible that it may be stable even at the temperature of molten magmas. Pirsson, in discussing this question, relies mainly

[1] *Doelter*, Physikalisch-Chemische Mineralogie, p. 177.
[2] For bibliography, see *Evans*, Quart. Journ. Geol. Soc., lvii. 38, 1901.
[3] Géologie Expérimentale, p. 179.
[4] Ancient Volcanoes of Great Britain, ii. 189.
[5] *Barus*, Amer. Journ. Sci., vi. 270, 1898; vii. 1, 1899; xli. 110, 1891.
[6] *Lemberg*, Zeit. d. Deut. Geol. Gesell., p. 588, 1887.
[7] *Friedel*, Bull. Soc. Min., xix. 14, 94, 1896.

upon the freshness of the other minerals present in the analcime-bearing rock; but this argument is not by any means conclusive, since a dehydrated analcime glass might again become hydrated after consolidation of the rock, without any appreciable alteration of the other minerals. The possibility of this reaction was examined by Loewinson-Lessing, who, however, failed to reproduce analcime by fusion in an atmosphere of water vapour.[1]

Upon the whole, therefore, the question of primary analcime is not definitely proved, although its possibility is not precluded by physical considerations if the influence of water under pressure is taken into account.

Hydrolysis.—It is necessary to consider also the influence of hydrolysis in the production of hydrated minerals. Hydrolysis plays an important part in geological chemistry. This process depends probably upon the extent to which water is dissociated into its ions, $\overset{+}{H}$, $\overline{OH}$. Attempts have been made to estimate this by Kohlrausch, Wijs, and Ostwald, with fairly concordant results.[2] The ionization of water appears to increase with its temperature, and this may explain the increased chemical activity of water at high temperatures.

Hydrolysis probably occurs in many cases where salts are deposited from solution. Thus magnesium chloride is hardly ever obtained in a pure state by the evaporation of its solution, owing to the hydrolytic reaction:

$$MgCl_2 + 2H{\cdot}OH = Mg(OH)_2 + 2HCl.$$

Where the mass of water is considerable and mineral composed of weak acids are present, hydrolysis generally takes place to a certain extent.

[1] Studien über die Eruptivgesteine, p. 100.
[2] *Whetham*, Theory of Solutions, p. 358.

Clarke has shown that many natural silicates give alkaline reactions when treated with pure water.[1] Cameron has pointed out the possibility of similar reactions in the case of aluminates and ferrates.[2]

Steam at high pressures can decompose the salts even of strong acids. The exhalations from volcanoes completely decompose ferric chloride, as follows :

$$Fe_2Cl_6 + 6H_2O = Fe_2(OH)_6 + 6HCl.$$

If the temperature is high, ferric oxide is formed thus :

$$Fe_2Cl_6 + 3H_2O = Fe_2O_3 + 6HCl.$$

Similarly, in volcanic regions the action of water upon boric acid forms sassolin.

It is to hydrolysis that may be referred the existence of certain basic minerals in Nature; and partial hydrolysis gives a reason also for the existence of water of crystallization and water of constitution in the same mineral.

An example of this kind has been described by Hayes,[3] in explanation of the formation of bauxite deposits. By the action of sulphuric acid, derived from the oxidation of pyrites, upon aluminous shales, alum and aluminium sulphate are formed. Aluminium sulphate is easily converted by hydrolysis into the basic salt, which, on contact with air, readily changes to the gelatinous aluminium hydroxide.

Influence of Pressure on the Dissociation of Hydrates. — The influence of pressure upon the dissociation of hydrates depends upon the volume change involved in the reaction. The experiments of Spring and Van 't Hoff[4] upon the double acetate of copper and calcium, which is a hydrated salt with six

[1] Journ. Amer. Chem. Soc., xx. 739-742, 1898.
[2] Sixty-fourth Report U.S. Dep. Agric., p. 169, 1900.
[3] Twenty-first Annual Report U.S. Geol. Surv., p. 461.
[4] Zeit. f. Phys. Chem., i. 227, 1887.

molecules of water, show that this salt, under a pressure of 6,000 atmospheres, has its transition point lowered from 76° C. to 40° C. Spring also showed that the hydrated arsenic trisulphide, which has a considerable vapour pressure, and can be decomposed into anhydrous sulphide and water at ordinary temperatures *in vacuo*, is readily decomposed by a pressure of about 6,000 atmospheres, with a contraction in volume of nearly 5 per cent.[1] There is an apparent anomaly in this case, which Spring explains by the assumption that the water in the hydrate is in the solid state—*i.e.*, as ice.

The influence of pressure upon the transition points of hydrates in the presence of water is generally in the opposite direction—that is to say, the transition temperature is raised by pressure. Little is known about this, but as far as evidence goes, the influence of pressure is extremely small. Thus Van 't Hoff states that in the case of the Stassfurt salts a pressure of 180 atmospheres, corresponding to a depth of 1,500 metres, would only raise the formation temperature of tachhydrite, $CaCl_2.(MgCl_2)_2.12H_2O$, from 22° C. to about 25° C. This is quite an insignificant amount in view of the fact that the range of temperature during the formation of the Stassfurt salts may have exceeded 50° C.[2]

In considering the volume change in dehydration, it is necessary to state whether all the products remain *in situ*, or whether liberated water can escape. Van Hise explains the dehydration which occurs in rocks at comparatively low temperatures to the effect of pressure in squeezing out the water.[3] This should, in general, only occur where definite hydrates are no

[1] Zeit. f. Anorg. Chem., x. 185, 1895.

[2] *Van 't Hoff*, "Physical Chemistry in the Service of the Sciences," Chicago University Decennial Publications, xviii. 1903.

[3] Treatise on Metamorphism, p. 178.

concerned. All definite hydrates have a fixed transition point for each pressure, and only undergo dehydration when their vapour pressure exceeds that of the superincumbent water vapour. This important point is often ignored in the consideration of geological changes. In the case of minerals under great pressure, when expansion cannot take place, hydration may be checked even when the aqueous vapour tension exceeds the dissociation pressure of the possible hydrate.

Hydration and Dehydration in Nature. — The velocity of hydration of anhydrous salts depends not only upon conditions of temperature and pressure, and the composition of the aqueous solutions in contact with them, but also upon their solution tension, as stated by Cameron and Seidell.[1] The velocity of dehydration has been found to be nearly proportional to the tension of water vapour in the salt, provided that the vapour is simultaneously removed from the surrounding atmosphere.[2]

From what has been already stated concerning the dissociation pressure and transition points of hydrous substances, it follows, as Heim has shown, that hydration is, as a general rule, characteristic of the upper portions of the earth's crust. Thus opal, or hydrated silica, is common in rocks which have been subjected to the action of meteoric waters, but is rare in unweathered rocks in plutonic regions. Diaspore, $Al_2O_3.H_2O$, and gibbsite, $Al_2O_3.3H_2O$, which occur as products of weathering near the surface, would be represented by corundum at greater depths. Complex hydrous silicates, such as kaolin, serpentine, and zeolites, were observed by Van Hise in the upper weathered portions of the Marquette region of Lake

[1] Journ. Phys. Chem., v. 643, 1901.
[2] *Richards*, Zeit. f. Anorg. Chem., xvii. 165, 1898.

Superior, and give place, at greater depths, to anhydrous silicates, such as muscovite, andalusite, garnet, and staurolite.[1] The felspars show similar phenomena. Albite may pass into analcime or natrolite, and anorthite into thomsonite or gismondite.[2] In this connection it is interesting to note an example of a reversal of the process of hydration, which was observed by Harker in the Skye basalts. The lime zeolites and lime-soda zeolites occurring in the amygdales of these rocks have been dehydrated by contact metamorphism, and transformed into lime-soda felspars.[3]

The action of dry steam, as present in fumaroles and solfataras, seems to be less effective in producing hydrated minerals than that of water. Delesse found that dry steam, even at a pressure of 5 atmospheres, has no appreciable action on minerals, and Barus[4] noted that the felspar in the diabase of the Comstock lode is not influenced by the prolonged action of steam at 100° C. The stability of anhydrite in Nature is interesting. Possibly the slowness of change of this mineral may be connected with the higher degree of symmetry of the crystalline form of anhydrite, as indicated by Kelvin.[5] At Bex, however, anhydrite is converted into gypsum in the upper parts to a depth varying from 18 to 30 metres. The reverse change from gypsum into anhydrite may, as already indicated, take place, even in the zone of weathering, under the action of salt solutions.

The phenomena of hydration and dehydration, unless accompanied by a change of colour, do not attract attention. It is probable that these changes are as

[1] *Van Hise*, Mon. U.S. Geol. Surv., xxviii. 444-459, 1897.
[2] *Clarke*, Bull. U.S. Geol. Surv., No. 125, pp. 32-45, 1895.
[3] Tertiary Igneous Rocks of Skye, p. 51.
[4] School of Mines Quarterly, vi. 1-23, 1884.
[5] Popular Lectures and Addresses, ii. 428.

ommon as those which are conspicuous by reason of heir colour effects. The influence of temperature nd moisture upon the iron hydrates is well known. n the case of laterite in India, the yellow xanthosi- erite soon weathers to reddish-brown turgite, owing o dehydration.[1] In the hot and arid region of South California the soils are dark red in colour, the iron eing in the form of hematite instead of the hydrous orms, göthite or limonite. Dehydration also takes lace in the hot regions of the Southern Appalachians, vhere the air is comparatively humid. It is only the eeper portions of the soil which retain the iron in a ydrated form.[2] Similar phenomena have been noted n the Mesabi iron-ore district.[3] The occurrence of ed ferruginous sandstone in conjunction with layers ontaining brown hydrated ferric oxide is less readily xplained, but the dehydration of certain beds may ave been effected by contact with salt solutions, as in he case of gypsum already referred to above.[4] The morphous hydrated compounds, such as many of the ron hydrates, would be expected to be more sensitive o weathering processes than the crystalline hydrates, ince the former have no definite dissociation pres- ure, but follow the ordinary laws of a volatile liquid n the presence of its vapour.

[1] *Holland*, "The Constitution of Laterite," Geol. Mag., x. 65, 1903.
[2] *Van Hise*, Treatise on Metamorphism, p. 482.
[3] *Leith*, Mon. U.S. Geol. Surv., xliii. 262, 1903.
[4] *Cf. Brauns*, Chemische Mineralogie, p. 145.

## VI

### EQUILIBRIUM CONDITIONS OF POLYMORPHOUS FORMS

Many minerals occur in more than one crystallin form. At any given temperature and pressure on of these forms is, in general, metastable with regar to the other, and the metastable form tends to pas spontaneously into the more stable variety. Thes polymorphous forms differ not only in their crystal line form and symmetry, but also in their specifi gravity, melting point, and other physical properties It is possible, also, that they may differ in molecula weight, the denser varieties being polymerized to greater or less degree. The passage from one form t another is, therefore, marked by a distinct volum change, with a corresponding absorption or release o energy. Theoretically, it would be inferred that th denser forms are more stable under high pressures and *vice versâ*. Similarly, the action of heat would b expected to promote the formation of the one possess ing the greater volume.[1]

Polymerism.—The part which polymerism plays i connection with polymorphism possesses geologica interest, especially with regard to the effects produce by what is generally known as dynamical metamor phism. The result of statical pressure will be toward the production of those combinations in which th molecules occupy the smallest space.

[1] *Cf. Tutton*, Science Progress, i. 109, 1906.

There is much uncertainty as to what is the real cause of polymorphism. Taking, for example, the familiar case of calcite and aragonite, we are at present ignorant as to whether these two forms of calcium carbonate owe their difference to the grouping of the molecules or to the arrangement of the atoms.[1] Clarke has given reasons for assuming an extensive polymerism of the silicates.[2] Vogt and others conclude that polymerism is confined to minerals crystallizing under considerable pressure, and that under ordinary atmospheric conditions the simpler molecular grouping will occur.[3] The view that pressure tends to the formation of complex molecules seems to throw light upon problems of metamorphism, and of the restriction of certain minerals to particular types of rock.

For the present, therefore, we regard polymorphism as a consequence of different equilibrium conditions between the interatomic or intermolecular forces by which crystalline forms are presumed to be held together. A certain grouping, which is stable at one temperature or pressure, is unstable at another, and tends to pass into a different arrangement.[4] The rearrangement of molecules which this process implies may explain the tendency to lag which is often exhibited in the course of mineral transformations. The cause of this lag is probably to be found in internal molecular friction, and in this case the more complex molecules would be more affected than those of simpler constitution.

Monotropic and Enantiotropic Substances. — In the change from one form to another the transition

[1] For further discussion of this question, see *Barlow* and *Pope*, Trans. Chem. Soc., pp. 89, 1675, 1906; pp. 91, 1150, 1907; also vol. xciii., 1908.

[2] Bull. U.S. Geol. Surv., No. 125, 1895.

[3] Silikatschmelzlösungen, i. 41.

[4] *Tutton*, Science Progress, i. 109, 1906.

point is sometimes at a temperature which is below the melting point of either form. In this case, the change from one form to another can take place in either direction. Such substances are called enantiotropic. Examples occur in the case of rhombic and monoclinic sulphur, in wollastonite and pseudowollastonite, and in other substances.

When the inversion point lies above the melting point, the change can only proceed in one direction. In this case one form is more stable than the other at all temperatures below the fusion point.[1] The unstable form may then change directly into the other over a considerable range of temperature, but the reverse change cannot be brought about. These substances are called monotropic. There is here, therefore, no definite inversion point. Some substances, however, possess what is called pseudo-monotropy, in which case the change can only be made to proceed in one direction, even although the inversion point lies below the melting point.[2] According to Tammann and Roozeboom, diamond and graphite are examples of pseudo-monotropy.

We will now proceed to consider some examples of polymorphism in detail.

Sulphur.—The equilibrium conditions of rhombic and monoclinic sulphur have been studied by several workers.[3] An examination of their results not only forms a convenient basis for the discussion of the transformation of polymorphous substances in general, but has also a special interest from a mineralogical point of view on account of the fact that rhombic crystals of sulphur alone occur under natural conditions. The accompanying diagram (Fig. 10) represents

[1] *Ostwald*, Zeit. f. Phys. Chem., xxii. 313, 1897.
[2] *Roozeboom*, Die Heterogenen Gleichgewichte, i. 177.
[3] *Reicher*, Zeit. f. Kryst., viii. 593, 1894; *Tammann*, Ann. d. Phys. lxviii. 663, 1899.

approximately the stable conditions for the different phases at different temperatures and pressures. O is a triple point (temperature 95·5° C.) at which rhombic sulphur, monoclinic sulphur, and sulphur vapour can coexist in equilibrium. AO and BO are the vapour pressure curves of rhombic and monoclinic sulphur respectively. B is another triple point at which liquid sulphur, monoclinic sulphur, and sulphur vapour are in equilibrium. The transition point of rhombic and

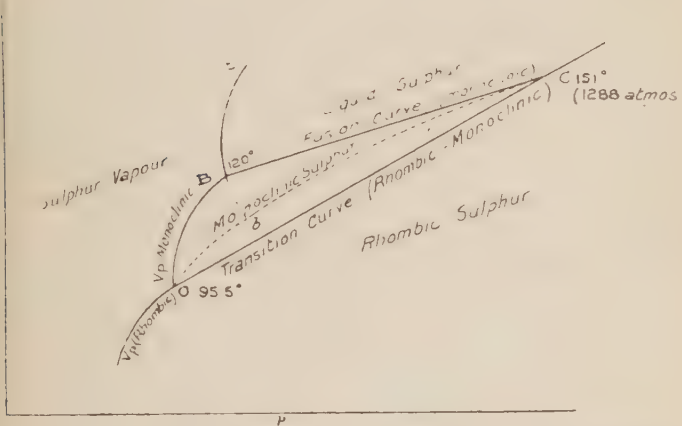



FIG. 10.—EQUILIBRIUM CONDITIONS OF RHOMBIC AND MONOCLINIC SULPHUR.

monoclinic sulphur is raised by pressure by an amount equal to about 0·05° C. for each atmosphere. The fusion curve of monoclinic sulphur is also raised by pressure, but to a smaller degree, hence the curves BC and OC cut. This gives another triple point, which was predicted by Roozeboom[1] and was realized by Tammann.[2] Hence, at 151° C., and at a pressure of 1,288 atmospheres, liquid sulphur on cooling would

[1] *Roozeboom*, Rec. Trav. Chim. Pays-Bas, vi. 314, 1887.
[2] *Tammann, op. cit.* 271.

crystallize in the rhombic form instead of the monoclinic form.

The diagram shows why monoclinic sulphur would not be expected to occur in Nature at ordinary atmospheric pressure. Its stable existence is limited to the area included in the curvilinear triangle OBC. At temperatures below 95·5° C. the rhombic form is alone stable, hence crystals deposited by sublimation or from solution will be in the rhombic forms met with in natural crystals. Molten sulphur can only pass into rhombic crystals directly at pressures exceeding 1,288 atmospheres. Since, also, the transition point at which rhombic sulphur passes into monoclinic sulphur is below the melting point, this substance is enantiotropic, and the change from one form to another is reversible. Suspended transformation, however, may occur, and rhombic sulphur may, in the absence of the monoclinic phase, be heated above the transition point to its melting point at *b* (114·5° C.) without passing into the stable form. Similarly, monoclinic sulphur, when cooled below 95·5° C., only slowly passes into the rhombic form. This is an example of the persistence of a metastable phase such as is of common occurrence in Nature.

It is interesting to note that sulphur has two melting points—a metastable melting point at 114·5° C., and a stable melting point at 120° C. This property is also possessed by other substances. Only one form, however, melts within the region of its stable existence—viz., that form which is stable at the higher temperature. In order to procure the metastable melting point it is necessary to raise the temperature rapidly beyond the transition point, so that the transformation has no time to take place.

Reference may here be made to the remark made on

[1] *Roozeboom*, Die Heterogenen Gleichgewichte, i. 109, 110.

p. 8 that it is doubtful whether the melting point of quartz has ever been realized.

Wollastonite and Pseudo-Wollastonite. -Somewhat similar to the example given above is the behaviour of the crystalline forms of calcium metasilicate, wollastonite, and pseudo-wollastonite. In Nature wollastonite occurs in tabular monoclinic crystals; but from quickly cooled slags Vogt obtained an apparently hexagonal calcium metasilicate, the nature of which has been recently studied by Allen and White.[1] They found that wollastonite at 1180° C. passes, with but slight alteration of volume, into this hexagonal form, which they have termed pseudo-wollastonite. Its melting point is 1512° C., whereas wollastonite melts at 1250° C. Since the inversion point at which pseudo-wollastonite is transformed into wollastonite is 1180° C., the occurrence of pseudo-wollastonite in quickly cooled slags is another instance of suspended transformation, and persistence of a metastable phase below the transition temperature. It is possible that the sulphur diagram given above would apply in a general sense to these polymorphous forms of calcium metasilicate, and the absence of pseudo-wollastonite in Nature will then correspond to the absence of monoclinic sulphur. Wollastonite is, therefore, an enantiotropic substance, with a reversible transformation at 1180° C. The comparative stability of pseudo-wollastonite in slags, when once the critical temperature has been passed, depends upon the small reaction velocity at temperatures below the inversion point. In the same way Reicher found that at a temperature of −35° C. monoclinic sulphur takes 500 times as long to pass into the rhombic form as at 0° C.[2] If the slag is quickly chilled to a glassy form

[1] Amer. Journ. Sci., xxi. 90 *et seq.*, 1906.
[2] See *Bancroft*, The Phase Rule, p. 31.

and slowly raised to a dull red heat, wollastonite is formed instead of the pseudo-mineral. It may therefore, be concluded that in those cases in which wollastonite has formed in Nature from fusion the temperature of formation was below 1180° C., and the same may be said of the occurrence of this mineral in certain metamorphic limestones. It is not necessary therefore, to explain the absence of pseudo-wollastonite in Nature as a result of the influence of pressure, as Morozewicz has suggested.[1]

Quartz and Tridymite.—The specific gravity of quartz is 2·66, while that of tridymite is 2·3. Hence Mendeléef suggested that their molecular volumes are different,[2] and that polymerization occurs in the transformation of one form into the other. Quartz readily passes into tridymite on heating under normal pressure. Thus tridymite separates in a bead of silica fused in microcosmic salt.[3] When quartz is rapidly heated, it may be made partially to fuse at the melting point of quartz, which is apparently lower than that of tridymite. Possibly this explains the discrepancy in the results obtained for the melting point of silica which Joly found to be 1200° C., and Boudouard found to be 1830° C.[4] The melting point of tridymite is always realized when quartz is slowly heated. The inversion point of quartz and tridymite has been recently studied by Day and Shepherd.[5] Quartz cannot be crystallized from simple fusion because of its viscosity. In the presence of potassium and lithium chlorides or sodium tungstate, powdered glass, when fused, gives crystals of quartz at temperatures below

[1] *Doelter*, Physikalisch-Chemische Mineralogie, p. 29.
[2] Principles of Chemistry, ii. 99 *et seq.*
[3] *Brauns*, Chemische Mineralogie, p. 21.
[4] *Joly*, Rep. Brit. Assoc., p. 730, 1900; *Boudouard*, Journ. Iron and Steel Inst., p. 350, 1905. See also Amer. Journ. Sci., xxii. 27, 1906.
[5] Amer. Journ. Sci., xxii. 275, 1906.

760° C. At higher temperatures tridymite is formed. Conversely, tridymite, fused in the presence of the same substances, passes into quartz at temperatures below 730° C. The transition, however, is not so easily effected as the reverse change, on account of the small reaction velocity of tridymite. Thus the inversion is typically enantiotropic. If we assume that the inversion point is not greatly lowered by the presence of the other substances, we arrive at the result that at temperatures below 760° C. quartz is the stable form, and at higher temperatures tridymite is the stable form. These results have been confirmed in the main by Quensel.[1] The apparent stability of tridymite at ordinary temperatures is explained by its reluctance to change at temperatures far removed from its inversion point. Bauer claims to have produced both quartz and tridymite side by side at a temperature of 120° C.[2] This apparently anomalous result, which would only be expected to occur at the transition temperature, has since been confirmed by Königsberger and Müller, who produced simultaneously quartz, tridymite, opal, and chalcedony by heating glass and obsidian in a bomb with water and carbon dioxide.[3] These results are supposed to be in harmony with Van 't Hoff's rule that high valency favours the existence of labile phases.

From a geological point of view these facts are highly interesting. The restriction of tridymite to the eruptive rocks is well known, and even in these it is not common. It may be concluded that the plutonic rocks have consolidated at temperatures below 760° C. The comparative scarcity of tridymite in the eruptive rocks may be due to a transition into quartz in

[1] Centr. f. Min., pp. 657, 728, 1906; also Geol. Mag., iii. 118, 1906.
[2] Zeit. f. Phys. Chem., xlii. 575, 1903.
[3] Centr. f. Min., pp. 339, 353, 1906.

many cases, as cooling proceeds below the inversion temperature. That this transition does take place at low temperatures has been noted by Boeris[1] and others.[2]

The Aluminium Silicates.—Similar relations exist between cyanite, sillimanite, and andalusite. The specific gravity of sillimanite is 3·23, while that of cyanite is 3·56 to 3·69. Vernadsky found that both andalusite and cyanite, when heated to a temperature lying between 1320° C. and 1380° C., pass into a fibrous aggregate of sillimanite crystals.[3] There seems to be, therefore, a definite inversion point, and cyanite becomes metastable at high temperatures. An interesting example of the conversion of cyanite into sillimanite as a result of contact metamorphism was noted by Barrow in the South-Eastern Highlands.[4] We have possibly here, therefore, an index to the temperature to which these rocks were raised by the igneous intrusion which induced the metamorphism. The change from cyanite to sillimanite may, therefore, be of practical value in field geology as indicating the proximity of an intrusive mass.

Calcite and Aragonite.—The two crystalline forms of calcium carbonate possess an especial interest in geology on account of their widespread occurrence in Nature. The rhombohedral form calcite has a specific gravity of 2·72, while that of the orthorhombic form aragonite is 2·94. The molecules of the latter may be polymerized as suggested by Genther.[5] Calcite, with the greater specific volume, is the more stable form at ordinary pressures and temperatures. Nevertheless, aragonite seems to persist in a very stable state of

[1] Riv. d. Min. (Padua), xxii. 66-80, 1899.
[2] Quart. Journ. Geol. Soc., lvii. 214.
[3] Zeit. f. Kryst., xxxix., 1904.
[4] Quart. Journ. Geol. Soc., xlix. 340, 1893.
[5] Ann. Chem., ccxviii. 288 *et seq.*, 1883.

ccount of its extremely slow rate of transformation. Boeke[1] has recently measured the inversion temperature of aragonite, which is said to pass slowly into alcite at about 470° C., without appreciable loss of arbon dioxide. The reverse change was not realized, robably owing to the slowness of transformation. Thus, the process appears to be monotropic, but is nore probably an example of pseudo-monotropy, as n the case of diamond. Aragonite has greater energy han calcite. The energy difference was found by Le Chatelier to be 6 g. cal. per gramme at 20° C., at vhich temperature the volume of 1 gramme is 0·367 c.c. or calcite and 0·340 for aragonite. At a dull red heat ragonite was found by Le Chatelier to pass into alcite with an absorption of 300 calories.[2] Van Hise, owever, regards the transformation as possibly exothermic,[3] as also does Foote,[4] while Boeke found an xtremely small heat effect. The transformation of ragonite into calcite was first noted by Haidinger,[5] nd was confirmed by Rose,[6] Mallard,[7] and Klein.[8] The latter showed that the transition apparently egins at about 150° C., proceeding very slowly and nly becoming complete at about 400° C. Tammann uggests that the conditions of equilibrium between alcite and aragonite may resemble the known conitions of transformation of the two crystalline modications of phenol.[9] Upon this assumption (see Fig. 11), AC would represent the limit of false equilibrium etween calcite and aragonite at low temperatures. Since calcite has the larger volume, this curve will

[1] Zeit. f. Anorg. Chem., xl. 245, 1906.
[2] Comptes Rendus, cxvi. 390, 1893.
[3] Treatise on Metamorphism, p. 245.
[4] Zeit. f. Phys. Chem., xxxiii. 740, 1900.
[5] Pogg. Ann., xi. 177, 1827.
[6] *Ibid.*, xlii. 361, 1837.
[7] Neues Jahrbuch f. Min., ref. in Zeit. f. Kryst., vii. 163, 1881.
[8] Zeit. f. Kryst., xi. 333.
[9] Krystallisieren und Schmelzen, p. 113, 1903.

rise with increase of pressure. Similarly, at higher pressures the curve CB represents the limit beyond which calcite will be transformed into aragonite although this transformation has not yet been realized.

Such a supposition might explain many cases in geology in which two crystalline forms of a polymorphous mineral are apparently both stable, and are capable of existing together, even in contact, at ordinary temperatures without any apparent transition taking place; and it is not at first obvious which modification

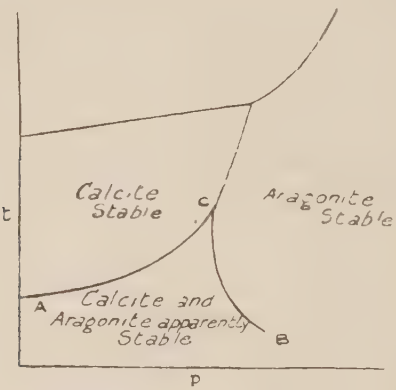



FIG. 11.—HYPOTHETICAL STABILITY DIAGRAM OF CALCITE AND ARAGONITE.

is to be regarded as the stable, and which the meta stable, form. The occurrence in Nature of both calcite and aragonite is in itself a proof of the extreme slowness with which the transformation of aragonite to calcite takes place at ordinary temperatures. It is significant, however, that aragonite does not usually occur as a constituent of highly metamorphosed rocks, possibly owing to the temperature during metamorphism having exceeded the transition point of 470° C.

The conditions which favour the formation of aragonite are to some extent known. Rose long ago

stablished the fact that aragonite often appears in ot solutions, while calcite is formed in cold solutions. oote[1] has suggested that the formation of aragonite n Nature may depend upon the velocity of crystallization. This view is supported by laboratory experiments. For example, aragonite is precipitated from hot solution of calcium chloride on addition of mmonium carbonate. The same solution in which ragonite is formed can be made to deposit calcite by aking the reaction sufficiently slow. Credner has hown that the appearance of aragonite may also be ontrolled to some extent by the concentration of the olution. Thus, while calcite is precipitated from a oderately strong solution, aragonite appears if the olution is more dilute.[2] At a certain temperature lso both calcite and aragonite are precipitated simulaneously, and this has occurred in Nature in the ematite districts of Cumberland.[3] The influence of o-solutes, also, sometimes determines the crystalline orm of the precipitated calcium carbonate.[4] On the vhole the facts seem to be in accordance with Ostwald's aw of successive reactions. The most stable form is ot always formed at once, but an intermediate metatable form may first appear.[5] There are many factors vhich appear to determine the formation of metastable odifications, and the subject is still obscure.[6]

It is interesting to note that calcite and aragonite orm an exception to the very general rule that the ore stable modification has the higher specific gravity. his may be a consequence of the higher degree of ymmetry of the calcite crystal.

[1] Zeit. f. Phys. Chem., xxxiii. 740, 1900.
[2] Neues Jahrbuch f. Min., p. 288, 1871.
[3] *Rudler*, Handbook to Collection of Minerals of the British Isles, . 150, 1905.
[4] *Brauns*, Chemische Mineralogie, p. 156, 1896.
[5] Principles of Inorganic Chemistry, p. 207 *et seq.*
[6] See *Schaum* and *Schönbeck*, Ann. d. Phys., viii. 652, 1902.

Other Polymorphous Minerals.—There are many other examples of polymorphous minerals of geological interest, but little is known of their equilibrium conditions. In the case of graphite and diamond, for example, the transition point can apparently only be realized under high pressure. Carbon crystallizes from solution in iron, under atmospheric pressure, in the form of graphite; but under high pressure Moissan has shown that carbon crystallizes from solution in iron in the form of diamond.[1] At a temperature in the neighbourhood of 3000° C. diamond passes into graphite. Since the fusion point of carbon is very much higher than this temperature, the reverse transformation from graphite to diamond would be expected to take place; but as this has not been realized, this may be a case of pseudo-monotropy, as stated above.

The oxides of titanium present an interesting group of polymorphous minerals. In some cases these appear in Nature as pneumatolytic minerals, and they have been produced artificially as a product of reaction between titanium fluoride and water vapour. Hautefeuille found that at a red heat rutile is formed, but brookite and anatase are produced at lower temperatures. Nothing is known of the transition points of these minerals. Both by reason of its symmetry and specific gravity, it may be inferred that rutile is the more stable form; and this conclusion is partly confirmed by mineralogical observations, since rutile pseudomorphs after both brookite and anatase are known. The three forms show a remarkable tendency to occur together in Nature, a phenomenon which is unusual with polymorphous minerals, although not altogether unknown in the case of other species, as for example, calcite and aragonite already referred to.

The dimorphism of iron pyrites, which occurs in

[1] Comptes Rendus, cxvi. 218-224.

Nature both as marcasite and pyrite, has been explained by Weinschenk as due to polymerism.[1] Here, again, both from its crystalline symmetry and specific gravity, pyrite is indicated as the more stable mineral. From the circumstance that marcasite is the characteristic form in sedimentary rocks, while pyrite occurs in plutonic rocks, Van Hise infers that marcasite is transformed into pyrite by pressure. The transition, however, does not appear to have been realized in the laboratory, and nothing is definitely known of the conditions under which it takes place. Stokes has noticed that much of the fibrous mineral usually called marcasite consists actually of pyrite.[2] It is possible that marcasite, like triclinic sulphur, undergoes a slow transformation into the more stable form of pyrite at ordinary temperatures and pressures. It is difficult, however, to account for the remarkable twin crystal consisting of a cube of pyrite interpenetrated by orthorhombic twins of marcasite, described by Trechmann from Westphalia.[3]

The Amphibole and Pyroxene Series.—One of the most interesting, and at the same time most obscure, examples of apparently dimorphous substances is that which is presented by the minerals included respectively under the hornblende and augite series. Tschermak has suggested that the hornblende molecule is polymerized as below:[4]

$$\text{Pyroxene} = R''_2(SiO_3)_2.$$
$$\text{Hornblende} = R''_4(SiO_3)_4.$$

Clarke, on the other hand, comes to a different conclusion, and assumes the pyroxene molecule to be double that of amphibole.[5] Vogt, in discussing the

[1] Zeit. f. Kryst., xvii. 501, 1890.
[2] Bull. U.S. Geol. Surv., No. 186, 1901.
[3] *Miers*, Mineralogy, p. 94.
[4] Tschermak. Min. u. Pet. Mitt., 1871, etc.
[5] Bull. U.S. Geol. Surv., No. 125, 1895.

general question of polymerization, assumes that pyroxene has the more simple molecule, as it can be prepared readily from artificial slags, whereas the amphiboles cannot be formed artificially from fusion.[1]

The question is still further complicated by the fact that hornblende and augite each form mix-crystal series of very diverse chemical constitution. The passage from augite to hornblende, perhaps as a result of pressure, is illustrated abundantly in the phenomena of uralitization and the formation of epidiorites. Yet, contrary to the rule that pressure promotes the formation of the denser variety, the specific gravity of the hornblendes is, on the whole, apparently lower than that of the pyroxenes. The transition of hornblende into augite is readily effected by simple fusion, as is well known.

Hornblende is, as a rule, a more common constituent of the plutonic rocks than augite; but hornblende also occurs in lavas. Streng records it as occurring in the vesicular cavities of the dolerite of Londorf, in association with tridymite, whereas neither of these minerals occurs in the rock itself.[2] Still more striking is the observation of Van Hise of secondary enlargement of hornblende crystals in the volcanic tuff of Kekekabic Lake.[3] That the hornblende of many andesites separated before the lava was erupted seems to be proved by the frequency with which it presents an outer magnetite zone and other evidences of magmatic corrosion; but the significance of this fact is neutralized by its occurrence intergrown with augite in many localities, as in the Saltash greenstone,[4] in the

[1] On this point, see *Chrustschoff*, Neues Jahrbuch f. Min., ii. 86-90, 1891.
[2] Neues Jahrbuch f. Min., ii. 206, 1888.
[3] Amer. Journ. Sci., xxx. 231-235, 1885.
[4] *Teall*, British Petrography, p. 231.

Malvern camptonite,[1] in the augite picrite of Inchcolm Island,[2] and elsewhere. The observations of Heddle at Portsoy also are significant. Here in some parts of the same mass augite is the predominant mineral; in other parts hornblende occupies the same position. In many granitic rocks, also, pyroxene is older than amphibole, and forms the nucleus around which hornblende has developed. In other cases augite has formed at the expense of earlier hornblende forming rims of augite around hornblende nuclei.[3] A further illustration of the transition from hornblende to augite has recently been furnished by the observations of Smeeth with regard to the augite in the Kolar schists of India. The evidence in this case seems to show that the hornblende in schists of Dharwar age, originally derived from an augite-bearing rock, has been again converted into a green augite by the influence of a subsequent acid intrusion. The green augite has in some cases been again converted into hornblende.[4]

Becke, in a detailed examination of this question, concludes that as a general rule in deep-seated rocks hornblende forms in preference to augite; while in eruptive rocks augite is formed in the place of hornblende. Becke explains this by an ingenious diagram (Fig. 12) in which HH is the assumed transition curve of hornblende on a temperature-pressure diagram. Above this curve augite is the stable mineral; below it hornblende is stable. The exact position of this curve is somewhat arbitrary, owing to the absence of data further than the experiments of Chrustschoff[5] and the known behaviour of hornblende on fusion.

[1] *Groom*, Quart. Journ. Geol. Soc., lvii. 164, 1905.
[2] *Teall, op. cit.*, pp. 95, 96.
[3] *Washington*, Journ. Geol., April, May, 1896.
[4] Bull. Mysore Geol. Dep., No. 3, 1905.
[5] Bull. de l'Acad. des Sci. St. Petersb., xiii. 1890.

FF and SS are the liquidus and solidus curves respectively; that is to say, above FF the liquid phase is stable, and below SS the solid phase is stable. Between these two curves is the crystallization interval. If now cooling takes place under plutonic conditions, the pressure may remain high, and the cooling curve may be assumed to take the form AAA. If cooling takes place under eruptive conditions, the cooling curve will take a form BBB, in which the pressure at first falls rapidly. It is now easy to see that except at very high temperatures, when augite may be stable under

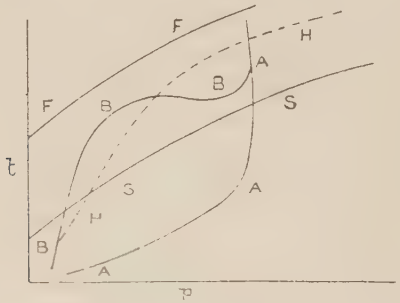



FIG. 12.—HYPOTHETICAL STABILITY DIAGRAM OF HORNBLENDE AND AUGITE. (AFTER BECKE.)

great pressure, hornblende will be the high-pressure mineral that will be formed. In eruptive rocks, on the other hand—viz., along the curve BBB—augite will be produced.[1]

By this hypothesis no attempt is made to explain the phenomena of any but primary occurrences. The case of secondary developments of either hornblende or augite is not considered. The difficulties which are presented by these minerals may possibly be connected with the fact that there is no difference between the pyroxenes and the amphiboles, so far as crystalline

[1] *Becke*, Tschermak, Min. u. Pet. Mitt., xvi. 327-336.

symmetry is concerned, and very little difference as regards specific gravity, two factors which usually influence in a marked degree the relative stability of polymorphous forms.

Magnesia Pyroxenes.—Before leaving this subject, attention may be drawn to the interesting results obtained by Allen, Wright, and Clement in their investigation of magnesium metasilicate.[1] These authors find that this substance is tetramorphic, and that the stable form, into which all the others pass at temperatures exceeding 1150° C., is monoclinic pyroxene. Thus enstatite should pass at this temperature into the monoclinic form, and the transition being monotropic, monoclinic magnesia pyroxene should occur as a constituent of igneous rocks. There are reasons to believe that this mineral does in fact occur,[2] but the temperature of formation of this mineral is rather higher than the probable consolidation temperature of most rocks.

[1] Amer. Journ. Sci., xxii. 385-438, 1906.
[2] *Cf. Judd*, Quart. Journ. Geol. Soc., xlii. 65, footnote, 1886.

## VII

### EQUILIBRIUM IN SOLUTIONS

It is convenient to define a solution so as to include not only the liquid, but also the solid and gaseous phases in contact with it. Van 't Hoff's definition is as follows: "A solution is a homogeneous mixture, the composition of which can undergo continuous variation within the limit of its stable existence."[1] Similarly, he defines a solid solution as a solid homogeneous complex of several substances, whose proportions may vary without loss of homogeneity.[2] Examples of such solid solutions have already been referred to in the case of silicate glasses and certain amorphous hydrates. Other cases are illustrated by mix-crystals, to be more fully discussed hereafter.

From the point of view of the phase rule, unsaturated solutions are tri-variant systems—that is to say, they possess three degrees of freedom. The conditions of equilibrium, therefore, can only be defined by three variable factors: pressure, temperature, and concentration. For the complete graphic representation of the equilibrium conditions of such systems triaxial diagrams are necessary.

Solubility Curves in Aqueous Solutions. — The monumental work of Van 't Hoff and his pupils in the determination of the conditions under which the

[1] Zeit. f. Phys. Chem., v. 323, 1890.
[2] *Ibid.*, p. 322.

Stassfurt salts were deposited[1] affords an instructive illustration of the general laws which govern the separation of salts from solution. In these investigations, in order to simplify the problem as far as possible, the influence of variable temperatures and pressures was eliminated by working at atmospheric pressure and at the constant temperature of 25° C.

Consider first the case of a single salt—for example, sodium chloride in solution. On evaporation, a concentrated solution is obtained, in which, at last, solid salt, solution, and vapour are in equilibrium.

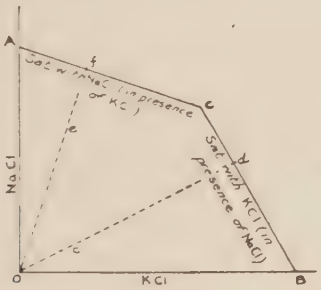



FIG. 13.—MUTUAL SOLUBILITIES OF SODIUM AND POTASSIUM CHLORIDES.

Whether the solid is pure salt or a hydrate does not alter the variancy of the system. If, however, two salts which do not react upon one another are present in solution, and are not in eutectic proportions, that salt which is in excess will separate first, and will continue to separate until the eutectic composition is reached.

In the diagram (Fig. 13) the molecular proportions of each salt in 1,000 molecules of water are represented

[1] The original papers were published in the Sitz. d. K. Akad. d. Wiss., 1897, and following years. A summary of his work by Van 't Hoff is given in "Physical Chemistry in the Service of the Sciences," Chicago University Decennial Publications, xviii., 1903.

on two axes at right angles to each other. The points A and B represent the solubilities of the two salts in pure water, viz. :

Solubility of NaCl : solubility of KCl : : 111 : 88.

AC represents the gradual decrease of solubility of NaCl in presence of increasing proportions of KCl. Similarly, BC represents the decrease of solubility of KCl in presence of increasing proportions of NaCl.

All solutions represented by points within the figure ACBO are unsaturated. Suppose the concentrations are represented by the point *c*. As evaporation proceeds, the relative proportions of the dissolved salt remain the same; but their concentration increases, the change corresponding to a motion along *cd*. At *d*, where the line BC is reached, the solution is saturated with KCl, which begins to separate. This diminishes the concentration of the KCl, and the change in concentration corresponds to a motion along *d*C. At C, which is a sort of eutectic point, a simultaneous separation of the two salts takes place in the proportions represented by the relative concentrations at this point—viz., 89 molecules of NaCl and 10 molecules of KCl. This, therefore, is the eutectic proportion of these salts.

In sea-water, NaCl is in excess of the eutectic proportion, the relative concentration of NaCl and KCl being represented by the point *e* in the diagram. On evaporation the change in concentration of these two salts is represented by a motion along *ef*, until AC is reached. Then NaCl begins to separate, and the concentration changes with further evaporation, by continued separation of NaCl, until the point C is reached when again the two salts will be deposited together in eutectic proportions.

In this case there are three components, two solids

and liquid, and four phases—viz., two solids, solution, and vapour. The system is, therefore, univariant. As the diagram shows, for a fixed temperature there is only one solution from which a simultaneous separation of NaCl and KCl can take place. All other saturated solutions are saturated with a single salt only.

The problem is more complicated when double salts can form, as, for example, in the case of KCl and $MgCl_2$. Sea-water contains these two salts in the molecular proportions of 22 molecules of KCl to 78 molecules of $MgCl_2$. The solubilities in 1,000 molecules of pure water are, for $MgCl_2$ 108 molecules, and for 2KCl 44 molecules. Let DA (Fig. 14) represent these proportions, as explained above. Let the point *c* represent the proportions of these two salts present in any solution. As evaporation proceeds, the concentration alters, as before, along *cd*. At *d* separation of KCl takes place, and the concentration alters then along *d*B. At B the solution is in equilibrium with KCl and with the double salt carnallite, $KCl.MgCl_2.6H_2O$; the latter, therefore, begins to separate.

Now, it is evident that, as the point B lies above the line bisecting the right angle at O, which line would represent equimolecular proportions of the two salts, the solution in equilibrium with carnallite and KCl contains more $MgCl_2$ in proportion to KCl than is represented by the equimolecular composition of the double salt. Therefore, a solution which is saturated as regards carnallite is supersaturated as regards KCl. For this reason, addition of water to solid carnallite will decompose it, with separation of KCl. Conversely, as carnallite separates at B in presence of solid KCl, and thereby causes a relative decrease in the concentration of KCl, this salt must redissolve in order to

maintain the constant proportions demanded by the conditions of equilibrium at the point B. Only when no solid KCl remains does the concentration again vary in the direction of BC. Along this line carnallite separates, and at the point C bischofite, $MgCl_2.6H_2O$,

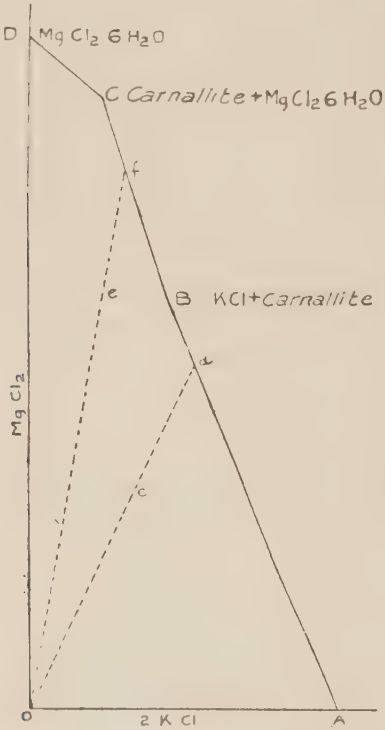



FIG. 14.—CARNALLITE DIAGRAM. (AFTER VAN 'T HOFF.)

begins to appear. Finally, the solution dries up, leaving a mixture of carnallite and bischofite.

This furnishes an example of resorption during isothermal crystallization. In the evaporation of a solution containing $MgCl_2$ and KCl in the proportions present in sea-water—viz., the proportions represented

by the point *e*—the diagram shows that at *f* carnallite alone separates, and the concentration varies along fC, until at C bischofite appears, as before.

Proceeding in a similar way, the conditions may be determined under which magnesium sulphate separates from sea-water.

Kieserite, $MgSO_4.H_2O$, occurs abundantly in the upper part of the Stassfurt deposits. From pure solutions this hydrate only forms at temperatures above 17° C., but in the presence of other salts its formation is possible at 25° C., the dehydration of the higher hydrate being brought about in the same manner as was explained in the case of anhydrite. At a greater concentration kainite, $MgSO_4.KCl.3H_2O$, is formed, and this is followed by carnallite and bischofite, as before.

The excess of sodium chloride in sea-water causes the latter to become saturated with this salt before the saturation limits of the magnesium and potassium salts are reached. It, therefore, separates on evaporation at a comparatively early stage, either as pure salt or as eutectic mixtures of definite composition. Van 't Hoff applied the same methods as are described above to the determination of the solubilities of the various salts—not in pure water, but in a saturated solution of sodium chloride. He thus reproduced the equilibrium conditions which prevail during the evaporation of sea-water.

Coming now to the lime salts, those being only slightly soluble in sea-water do not materially influence the general results. Calcium sulphate begins to separate before even sodium chloride, and appears first as anhydrite, and at greater concentrations in the form of various double salts, such as glauberite, $CaNa_2(SO_4)_2$; syngenite, $CaK_2(SO_4)_2.H_2O$; and polyhalite, $Ca_2MgK_2(SO_4)_4.2H_2O$.

It is possible now to follow the order of separatio as exhibited in the Stassfurt deposits. There are fou main regions, in the following descending order :

1. The carnallite region, characterized by massiv carnallite, with some rock-salt, bischofite, an kieserite.
2. The kieserite region, with abundant kieserit interstratified with some rock-salt and kainit
3. The polyhalite region, consisting mainly rock-salt, with thin seams of polyhalite.
4. The anhydrite region, consisting mainly rock-salt, with thin seams of anhydrite, and layer of anhydrite at the base.

During the deposition of the Stassfurt salts, ther fore, anhydrite was the first mineral to separate. Th was soon accompanied by rock-salt, which continue to separate throughout the whole mass, becoming les in quantity in the upper layers.

As concentration proceeded, pure anhydrite cease to separate, but various double salts appeared, givin place finally to polyhalite, into the composition which magnesium and potassium salts enter. Roc salt is still being deposited.

In the next stage the magnesium and potassiu sulphates, schönite, leonite, and also kieserite, appea rock-salt being deposited in smaller quantity. Lastl the chlorides of magnesium and potassium appear the carnallite region, in which rock-salt becomes st less conspicuous. This region contains also certa substances, such as bromides, which, by reason of the greater solubility or their small proportion, could n be deposited at an earlier stage.

Thus viewed broadly, and omitting minor detail we may recognize three stages in the minerals whi accompanied the deposition of rock-salt. These ar

n ascending order: (1) calcium sulphate; (2) magne-
ium sulphate; (3) magnesium and potassium chlorides.
Usiglio attacked the problem of the separation of
alts from sea-water by the actual evaporation on a
rge scale of water from the Mediterranean at Cette.[1]
he first substance to separate was calcium carbonate,
hich was present in larger quantity than usual in the
ample tested; then followed sodium chloride and
ypsum, mixed at a later stage with small quantities
f magnesium salts. As the mother liquor became
cher in magnesium salts the greater was the influence
f temperature upon the nature of the separating
ystals. At length a stage was reached at which
odium chloride was deposited by day and magnesium
ulphate by night. Finally, by pouring off successive
nother liquors he got from the first pouring a mixture
f sodium chloride and magnesium sulphate by day,
nd from the second pouring magnesium sulphate by
ight.

Usiglio did not succeed in reproducing the exact
equence occurring at Stassfurt. Thus he got little or
o anhydrite, and no polyhalite or kieserite. The
ctual process was not completely represented in his
xperiments. He was, however, the first to draw atten-
on to the important part which temperature plays in
he natural process.

Van 't Hoff also found that the conditions of equili-
rium at other temperatures were not the same as
hose which obtain at the constant temperature of
5° C. At certain temperatures salts appeared which
ere absent at 25° C. Thus hartsaltz, a mixture of
eserite, sylvine, and rock-salt, only separated at
5° C. Langbeinite appeared at 37° C., and loewite at
5° C. Certain salts, also, present at 25° C. no longer
ppeared if the evaporation was conducted at higher

[1] *Usiglio*, Ann. de Chim. et de Phys., xxvii. 92, 172, 1849.

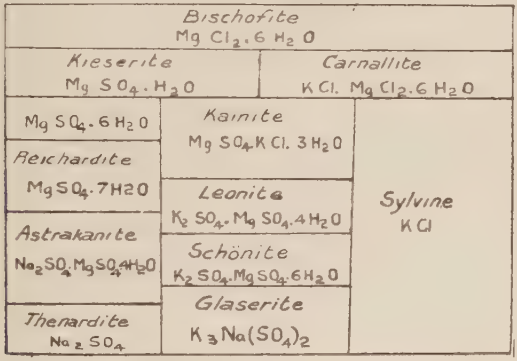
temperatures. Thus, at 47° C. reichardite, and 47·5° C. schönite, no longer appeared. Carnallite, als at 168° C., is decomposed, with separation of sylvine.

These observations explain certain phenomena whic have been observed in Nature. On the borders of th Caspian Sea, in summer, gypsum, rock-salt, and ma nesium sulphate separate, but in winter glauber sa or thenardite separate; and in spring and autum astrakanite ($Na_2SO_4.MgSO_4.4H_2O$) and rock-salt a pear.[1] These changes in the nature of the deposite salt lead to the expectation of the recurrence of se sonal and even diurnal variations in natural deposi of this kind, and explain the alternation of certa layers in the Stassfurt sequence. It is thus possib to determine to some extent the range of temperatu within which the Stassfurt salts were deposited. Thu tachydrite ($CaCl_2.2MgCl_2.12H_2O$) is incapable of e istence above 83° C.[2] The lowest temperature at whic certain salts are capable of existing in the presence other salts with which they are associated has als been determined. These are as follows: Glauberit 10° C.; langbeinite, 37° C.; loewite, 43° C.; loewi and glaserite, 57° C.; kieserite and sylvine, 72° C.[3]

The influence of time must also be considered. Th important factor is very difficult to control in labor tory experiments. Van 't Hoff considers that this the chief cause of the discrepancy between Usiglio results and his own. The former experiments we too rapid for geological processes, owing to the reta dation which results from supersaturation phenomen For this reason, certain substances may be entire missed in the process of artificial crystallization, an in fact, led in Van 't Hoff's experiments to the no

[1] *Brauns*, Chemische Mineralogie, p. 343.
[2] *Van 't Hoff* and *d'Aus*, Sitz. d. K. Akad. d. Wiss., pp. 913-916, 19
[3] *Van 't Hoff*, Zeit. Electrochem., xi. 709, 710, 1905.

ppearance of certain salts which theoretically should ave been formed. This was particularly the case vith certain calcium salts, as well as with leonite, ieserite, and kainite. Solutions from which these ubstances ought to have been deposited did not ecover from supersaturation even by slow crystalliza- ion. For this reason, the solubility method of Van 't Hoff gave better results than the crystallization method f Usiglio. The study of the Stassfurt salts, when xamined in the light of the equilibrium law, leads to mportant general conclusions regarding the separation




IG. 15.—Simplified Projection of a Space Model, illustrating the Formation of the Stassfurt Salts. (After Van 't Hoff.)

f salts from solution. By means of the space model onstructed by Van 't Hoff to represent the result of he isothermal evaporation at 25° C. of solutions of ea-salt, the successive changes in the character of the eposit can be followed. This space model shows that n general only three surfaces meet at a point. Hence ot more than three salts can in this case have been in quilibrium in a saturated solution.

Fig. 15 is a simplified form of such a space model, in vhich the different surfaces of the space model are epresented by rectangular areas on a plane surface.

This refers only to the results obtained at 25° C., an lime salts are excluded. At other temperatures th areas will be different, but the influence of the lim salts is comparatively unimportant on account of the small solubility.[1] Van 't Hoff suggests that this dia gram contains material for a great many geologic inferences as regards the paragenesis of natural salt It is only necessary to see whether the salts are i contiguous areas to determine the possibility of the co-existence at 25° C. Thus kieserite and sylvine coul not be deposited together at this temperature in th form of hartsalz. Yet hartsalz is present in the uppe part of the Stassfurt deposits. This apparent anomal has been explained by Meyerhoffer, who has show that at 70° C. the kieserite region on the diagram contiguous to the sylvine area. It might be conclude therefore, that hartsalz has been formed at this hig temperature. It is possible, however, that hartsa was formed by the action of water on a mixture kieserite and carnallite, magnesium chloride bein carried away in solution.[2] Similarly, it is seen by th diagram that glaserite can occur with astrakanite, bu not with bischofite.

The question naturally arises why rock-salt deposi in general do not always show the Stassfurt sequenc At Hanover, for example, the polyhalite and kieseri regions are wanting, while very many rock-salt bed contain no potassium salts and a very small proportio of magnesium salts. Yet these deposits are believe also to have been formed from sea-water. The reaso for this may be explained by the conditions und which the Stassfurt deposits were formed—*i.e.*, in a isolated basin cut off from the ocean, as suggested b

[1] *Van 't Hoff*, Physical Chemistry in the Service of the Sciences.

[2] Tschermak, however, shows that where carnallite is mixed wi kieserite it alters to kainite and bischofite, instead of sylvine, by t action of water.

Ochsenius.[1] The Hanover deposits may represent an overflow from that basin after the lime salts had separated. In many cases the basins remained in contact with the sea, and in them practically only gypsum or anhydrite and rock-salt would be formed, since each influx of sea-water would prevent the concentration of the mother liquor to the point at which the magnesium salts and carnallite would separate. Under these conditions, only the initial stage of the Stassfurt sequence would be reproduced. The actual condition of the Stassfurt deposits is complicated also by secondary reactions. Thus, as has been shown, sylvine results from the decomposition of carnallite, and kainite also forms from carnallite and kieserite.

Application of the Space Model to Igneous Magmas.—The study of the Stassfurt salts, and of the equilibrium conditions under which they were formed, suggests the possibility that similar methods of investigation might be successfully applied to rock magmas. Bauer has endeavoured to construct a space model upon experimental data to illustrate the separation of quartz and felspar from a molten magma.[2] He proceeded by determining the limits of saturation of a pure orthoclase magma with silica and potassium aluminate, $AlO_2K$. Two axes at right angles represent respectively the concentrations of silica and $AlO_2K$ (see Fig. 16), and the temperature is represented by a third axis, $T_1T_2$.

From his experiments he inferred that, starting, for example, with a concentration represented by the point D′ on the silica face, and assuming that the magma crystallizes in isothermal stages, by the evaporation of the volatile constituents, quartz will first separate, and the concentration will vary along

[1] Zeit. f. Prakt. Geol., p. 189 *et seq.*, 1893.
[2] Zeit. f. Phys. Chem., xlii. 567, 1902.

D'D, until at D the orthoclase field is reached, when quartz and orthoclase will crystallize together. The final result will be a quartz porphyry, with quartz phenocrysts in a ground mass of quartz and felspar. Within the field ACB only orthoclase separates, and quartz is resorbed, thus recalling the case described above of carnallite and sylvine. He thus explains the corrosion of quartz often noticed in this class of rock. In a similar way he illustrated the formation of aplite and pegmatite. An interesting point in Bauer's research was the importance attached to the influence

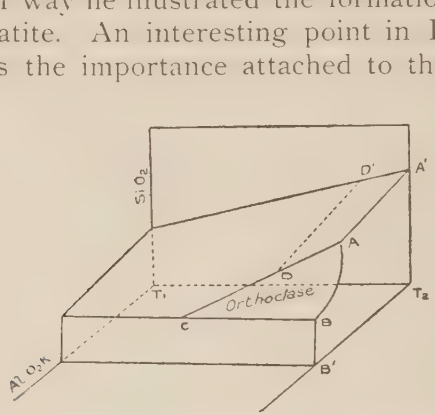



FIG. 16.—SPACE MODEL ILLUSTRATING THE FORMATION OF QUARTZ PORPHYRY. (AFTER E. BAUER.)

of water vapour upon the behaviour of the magma and upon the formation of the eutectic. The difficulties of this method of investigation are great, and the results are not sufficiently definite to form the basis of any generalization. *A priori*, however, it would appear that, as the influence of water vapour and other volatile constituents tends to lower the melting points of the magmatic constituents, the escape of these might in many cases promote isothermal crystallization. For this reason plutonic rocks might crystallize at lower temperatures than volcanic rocks. In the former case crystallization is more often

isochoric. The two processes may also proceed simultaneously, and the complexity of the problem is thus increased. Attempts to determine the mutual solubility of silicate minerals in one another have also been made by Lenarčič and Doelter, but the investigation is beset with many technical difficulties, and definite results have not been realized.[1]

Equilibrium of Two Liquid Phases.—The preceding remarks refer to the equilibrium of solutions in contact with solid phases. We have now to consider certain cases in which the solid phase is absent, and there are, instead of one homogeneous liquid phase, two or more mutually saturated solutions in equilibrium with one another. Liquids which are not miscible in all proportions are termed non-consolute. Until quite recently examples of two liquid phases were unknown, except in solutions of several components. Cases have now been investigated, however, in which there appears to be biphasic equilibrium between liquids in systems of one component only. Smith has found that liquid sulphur at certain temperatures separates into a pale yellow mobile liquid and a brown viscous liquid, which are only partially soluble in each other.[2]

When certain pairs of metals, such as zinc and lead, zinc and bismuth, lead and aluminium, bismuth and aluminium, or cadmium and aluminium, are melted together, they are found not to be miscible in all proportions. Thus, if the relative concentrations of such metals, A and B (Fig. 17), are represented along the abscissa, and the temperatures along the ordinate, the curve *xyz* represents the limits of a homogeneous solution. At all points outside the curve the mixture represents a reciprocal solution of one metal in the

[1] *Doelter*, Physikalisch-Chemische Mineralogie, p. 239.
[2] Journ. Amer. Chem. Soc., xxvii. 797, 979, 1905.

other in various proportions. At $z$ the metals are miscible in all proportions. Inside the curve there is a separation into two liquid layers of different compositions.[1] Similar phenomena are presented by mixtures of phenol and water,[2] aniline and water and other substances. In the case of nicotine and water Hudson found that at temperatures above 205° C. a homogeneous solution is formed when the mixture is in equal proportions. At 205° C. the liquid divides into a saturated solution of nicotine in water floating on the top of a saturated solution of water

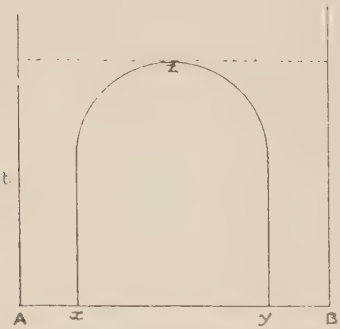



FIG. 17.—EQUILIBRIUM CONDITIONS OF NON-CONSOLUTE LIQUIDS.

in nicotine. At 90° C. these liquids change places and at 64° C. they mix again and become homogeneous. Similarly, an alloy of 43·64 parts of bismuth with 56·36 parts of zinc at a temperature between 700° and 800° C. separates into two portions, the heavier of which contains 84·82 parts of bismuth and 15·18 parts of zinc, and the lighter portion 2·47 parts of bismuth and 97·55 parts of zinc. These arrange themselves in the order of their specific gravities.

In the above cases it is seen that there is for such

[1] *Wright*, Proc. Roy. Soc., l. 390, 1892.
[2] *Rothmund*, Zeit. f. Phys. Chem., xxvi. 433, 1898.

iquids a critical solution temperature at which the iquids mix in all proportions. The same result, nowever, may often be produced by the addition of a third substance. Thus, an addition of 40 per cent. of silver prevents the separation of the mixture of bismuth and zinc described above. This property is well illustrated in the case of a mixture of chloroform and water[1] to which is added acetic acid. Chloroform and water are only partially miscible, but acetic acid mixes in all proportions with each of these substances. If the concentrations of these three substances are

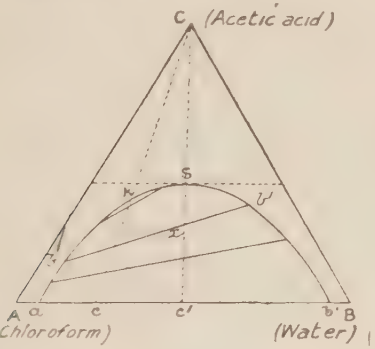



FIG. 18.—EQUILIBRIUM CONDITIONS OF PARTIALLY MISCIBLE LIQUIDS.

hown on a triangular diagram, as in Fig. 18, it is ound experimentally that a mixture of chloroform and ater divides into two solutions, with compositions epresented by the points $a$ and $b$ on the line AB. If, ow, acetic acid is added, the behaviour of a solution f the three substances having a composition repre-ented, for example, by the point $x$ within the curve $Kb$, will be to split up into two solutions having the ompositions represented by the extremities $a'$ and $b'$ f the tie-line $a'xb'$. At K the tie-lines vanish, and a

[1] See *Findlay*, The Phase Rule, p. 234.

homogeneous solution results. As long as the tota composition of the solution lies below the point S, tw liquid layers will be formed; but when sufficient aceti acid is present to raise the total composition above th point S, only one homogeneous solution will result Similar phenomena have been observed by Newth, when a strong solution of ammonia was shaken u with a saturated solution of potassium carbonate.

From these facts it is seen that non-consolute liquid may have not only a critical solution temperature a which they become miscible in all proportions, but als that complete miscibility at any temperature may b brought about by the addition of a sufficient amoun of a third substance in which each of the other tw are completely soluble.

Application to Magmatic Differentiation.—Th equilibrium conditions between two liquids which ar not miscible in all proportions suggest a fascinatin explanation of problems of magmatic differentiatio and this theory was first proposed by Durocher t explain the separation of magmas into partial magma insoluble in one another. The same theory forms th basis of the kern hypothesis of Rosenbusch, and ha also been elaborated by Arrhenius, Backström Loewinson-Lessing,[3] Becker,[4] and others. The fact already described support to some extent the con clusion that even chemically-related substances, whic are apparently consolute, may become non-conso lute under certain circumstances. Von Jüptner, fo example, explains the formation of mottled iron, whic is supposed to be a mixture of austenite and marten site, on the assumption that these substances represen two solid solutions, resulting from the solidification o

[1] Proc. Chem. Soc., April 5, 1900.
[2] Journ. Geol., iii. 773, 1893.
[3] Studien über die Eruptivgesteine.
[4] Amer. Journ. Sci., iii. 32, 1897.

wo partially miscible liquids.[1] In the separation of ulphides in the blast furnace the sulphides appear to livide themselves unequally between the two solvents —viz., metal and slag—in the proportion of the partition oefficient following Nernst's law of heterogeneous quilibrium. This ratio has been quantitatively letermined by Von Jüptner. Vogt has shown that ulphide ores are more soluble in basic than in acid nagmas, and if we assume a differentiation of a magma nto two parts mutually immiscible, the sulphide will e chiefly concentrated in the basic magma.[2] Vogt hus explains the phenomena of many deposits of ulphide ores, such as the association of sulphides vith gabbros and norites.[3] The tendency of sulphides o separate from fused silicates is believed by Vogt to e supported by the so-called globulites and margarites f Vogelsang, which occur in some blast-furnace slags. He finds these bodies to be not silicates, as Vogelsang elieved, but monosulphides of calcium, magnesium, tc., which separate from the silicates by reason of heir imperfect miscibility.[4]

Backström has advocated a similar theory to explain he separation of spheroidal segregations in magmas, nd also differentiation phenomena in general. Thus e regards the basic spheroids of Kortfors as the esult of fluid drops of basic magma in an acid matrix. The extreme differentiation, also, exhibited by the asalts and soda-liparites of the Iceland province, in vhich intermediate stages are apparently wanting, he scribes to the separation of a magma into two non-onsolute parts. Loewinson-Lessing extends this heory to many other phenomena, including com-

[1] *Von Jüptner*, Siderology, p. 130.
[2] *Vogt*, Silikatschmelzlösungen, i. 99, 100, 1903.
[3] Zeit. f. Prakt. Geol., 1893-1901.
[4] *Vogt*, Beiträge zur Kenntniss der Gesetze der Mineralbildung in chmelzmassen, p. 254, 1892.

posite dykes and banded gabbros. He has also considered the possible influence upon non-consolute magmas of a third substance in which they are completely soluble. He assumes, for example, a pyroxenite magma and a felspar magma existing in two non-miscible layers. If these each absorb silica at a certain temperature homogeneity may be re-established, but on further cooling separation may again take place, forming new partial magmas differing from the original non-miscible magmas.[1] If such results can take place, there is no limit to the variation which is thus made possible. Brögger has pointed out one of the chief difficulties which such a theory presents.[2] Any two liquids separating in this way and remaining for any length of time in a liquid state would arrange themselves in obedience to the laws of gravity. At Square Butte, however, and in other cases, heavy rocks rest upon others which are specifically lighter. Another objection is the sharp boundary line which would be expected to occur between the two differentiated portions. Such do occur, it is true, but they are comparatively exceptional. Then, again, there is the absence of any experimental evidence. Fused silicates have been abundantly observed both in the case of metallurgical slags and artificial glasses, but nothing pointing to separation into non-consolute portions has yet been recognized.

With regard to the above objections, however, it is necessary to distinguish between a density stratification in a magma basin and an arrangement according to density in an intruded or extruded igneous mass derived from such a basin. The influence of viscosity also might prevent a gravity stratification from taking place.

[1] *Loewinson-Lessing*, Studien über die Eruptivgesteine.
[2] *Brögger*, Ganggefolge des Laurdalits, p. 351.

Harker thinks that the principle of limited miscibility in rock magmas may extend, not only to mixtures of sulphides and silicates, but also to other substances.[1] Pratt's description of the mode of occurrence of corundum, in association with the peridotes,[2] suggests the view that alumina and olivine may be only partially miscible; while the seams of nearly pure picotite and chromite in the banded peridotites of Skye can only be explained by the simultaneous intrusion of partial magmas consisting respectively of spinel and peridotite. Certain other non-silicate minerals, such as apatite, may also possess this property.

This hypothesis has sometimes been advanced in order to overcome the difficulties of diffusion, but these difficulties still remain. Before a separation can take place into two liquids, the mixture must reach a definite homogeneous composition, which involves very complete diffusion.

[1] *Harker*, Natural History of Igneous Rocks, p. 200.
[2] Amer. Journ. Sci., vi. 49-65, 1898; viii. 227-231, 1899.

## VIII

### THE EUTECTIC THEORY

The study of alloys, such as those of gold and aluminium, shows that the first formed crystals, whether of a pure metal or of a metallic compound, are separated by channels of eutectic alloy, which solidifies at a lower temperature.[1] Natural ice, also, usually possesses a granular structure, consisting of pure ice crystals separated by a film of liquid residue, the latter consolidating only at the cryohydric point. These films of cryohydrate also contain bubbles of entangled air. When sea-water begins to freeze, the ice is at first a pasty mass of crystals mixed with brine, which may remain unfrozen for a considerable time. The more gradual the process of freezing, the less salt is entangled, and the more solid is the ice.[2] On melting a block of ice in the sun it may be gradually reduced to a heap of crystalline grains. Buchanan suggests that glacier flow is thus aided by channels of low freezing liquid between the solid ice crystals. These liquid films allow the ice to yield slightly to stress.[3] In the case of substances which are not mutually soluble—as, for example, sand and sulphur—the melting points will not be affected.

The Fusion Curve of Binary Systems.—In the case of a binary system consisting of two mutually

[1] *Ewing* and *Rosenhain*, Phil. Trans. A., p. 353, 1899.
[2] *Weyprecht*, Die Metamorphosen des Polareises, 1879.
[3] Proc. Roy. Soc. Edinb., xiv. 129, 1887.

oluble substances which do not react chemically, three ypes of fusion curve may occur when these are melted ogether in various proportions.

In the first case (Fig. 19) the fusion (or solubility) urve is a straight line joining the melting points of ne pure substances. This type arises when isomor-

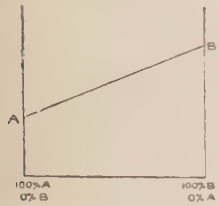



FIG. 19.—FUSION CURVE OF BINARY MIXTURES (FIRST TYPE).

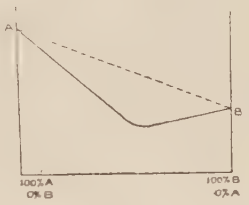



FIG. 20.—FUSION CURVE OF BINARY MIXTURES (SECOND TYPE).

hous mixtures of the two substances can occur etween all limits, as in the case of the gold-silver lloys. In this case the melting point of the more usible substance, A, is raised by the presence of the ther substance, B. In the second case (Fig. 20), at certain temperature, as at C, the mixture melts

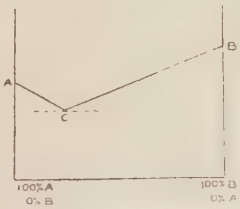



FIG. 21.—FUSION CURVE OF BINARY MIXTURES (THIRD TYPE).

t a minimum temperature; but the curve is con-inuous, and on cooling neither substance separates in he pure state. Examples of this type have only been ecognized in certain organic substances.

In the third type (Fig. 21) the two curves cut at an

angle at the eutectic point. On cooling a fused mixtur of this type the excess constituent, with reference t the eutectic composition, separates in the pure stat while at the eutectic point, C, a mixture of the tw substances separates in constant proportions. Com plexity is often introduced by the existence of mor than one eutectic. In the case of the lead-tin alloy there is only one eutectic, but the copper-zinc alloy have four, and the copper-tin alloys have at least si eutectics, and a very complicated set of conditions ma be set up on cooling.[1] Similarly, Day and Shepher found three eutectic points in the fusion curve o mixtures of lime and silica.

In the case of rock magmas these complex condition are often, if not always, present, and the application o the eutectic principle is rendered more difficult. Ther is, however, sufficient evidence that fused silicate follow the same laws, and behave in a manner simila to ordinary solutions, due allowance being made fo disturbing influences, such as viscosity, etc. Proo of the lowering of the melting point in magmas i sufficiently well established. Thus, Vesuvian lava are known to contain leucite, which has a meltin point of about 1420° C., and augite, with a meltin point of about 1200° C., is occasionally enclosed in i Evidently, therefore, in this case leucite must hav crystallized below its normal melting point.

Application to Aqueous Solutions.—It will b convenient, before considering further the theory o eutectics, to examine briefly the conditions of equ librium in certain systems which have been invest gated experimentally.

For the sake of clearness, it may be well to refe in the first place to Guthrie's well-known diagra (Fig. 22), illustrating the lowering of the freezing poi

[1] *Heycock* and *Neville*, Phil. Trans., cxciv. 201, 1900.

of water by the addition of sodium chloride.[1] This diagram enables us to realize quantitatively what will happen during the process of cooling solutions of this salt of any concentration through any range of temperature. Take, for example, the concentration denoted by the point D. At the point F the fluid phase is stable. As the temperature falls the curve OP is reached at E. This is the limit at which the fluid phase is saturated with respect to the solid phase, ice. Below this point the liquid is supersaturated with respect to ice, which accordingly begins to separate.

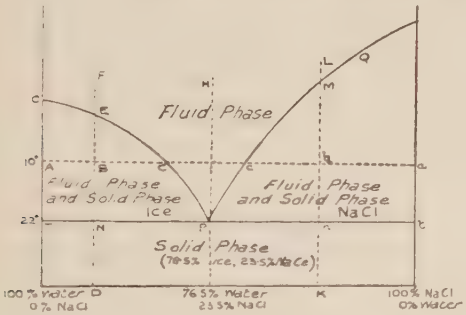

Fluid Phase
Fluid Phase and Solid Phase Ice
Fluid Phase and Solid Phase NaCl
Solid Phase (76.5% Ice, 23.5% NaCl)
100% Water 0% NaCl
76.5% Water 23.5% NaCl
100% NaCl 0% Water

FIG. 22.—FREEZING-POINT CURVE OF WATER AND SODIUM CHLORIDE.

At $-10°$ C. (namely, at B), the quantity of ice which will separate before equilibrium is restored will be as much as will alter the concentration to that of the point C on the equilibrium curve. We have, therefore, at this temperature the relation

$$\frac{\text{Solid phase (ice)}}{\text{Liquid phase (solution)}} = \frac{BC}{AB}.$$

Similarly, at $-22°$ C. the quantity of the ice that separates will be represented by the ratio

$$\frac{\text{Solid phase (ice)}}{\text{Liquid phase (solution)}} = \frac{NP}{NT},$$

[1] *Guthrie*, Phil. Mag., p. 359, 1876.

and the composition of the mother liquor alters to that denoted by the point P. Below this temperature the liquid phase disappears, and both ice and sodium chloride separate in constant proportions, consisting of 76·5 per cent. ice and 23·5 per cent. sodium chloride.

Similarly, if we follow the equilibrium conditions at another concentration, represented by K, along the temperature ordinate LM*n*K, on crossing the equilibrium curve QP at M sodium chloride begins to separate. At −10° C. the quantity of sodium chloride deposited will be represented by the ratio

$$\frac{\text{Solid phase (sodium chloride)}}{\text{Liquid phase (mother liquor)}} = \frac{bc}{ab},$$

and the composition of the mother liquor alters to that denoted by the point *c* on the equilibrium curve QP. At −22° C. we have

$$\frac{\text{Solid phase (sodium chloride)}}{\text{Liquid phase (mother liquor)}} = \frac{n\text{P}}{nt},$$

and the composition of the mother liquor alters to the eutectic composition at P. Below this temperature both sodium chloride and ice will again be deposited in eutectic proportions. At the concentration G, that of the eutectic, no separation takes place until the temperature −22° C. is reached, when the whole mother liquor solidifies in eutectic proportions as before. Thus the quantity, and also the character, of the solid phase which separates from solution is determined solely by the composition of the eutectic, which the mother liquor must ultimately reach. It is invariably the excess constituent which crystallizes—that is to say, that substance which is present in excess of the eutectic proportion. At the eutectic concentration the two substances crystallize together and the liquid phase disappears.

Application to Alloys.—The same principles have been found to apply to alloys. This may be illustrated by the lead-antimony alloys.[1] The diagram is represented in Fig. 23.

It is not necessary to recapitulate the details, which resemble precisely in principle those given above. Alloys containing less than 13 per cent. of antimony—as, for example, that represented by the point D—will deposit first lead, then, on reaching the temperature 247° C., a mixture of lead and antimony in eutectic proportions. This will result in a mass consisting of

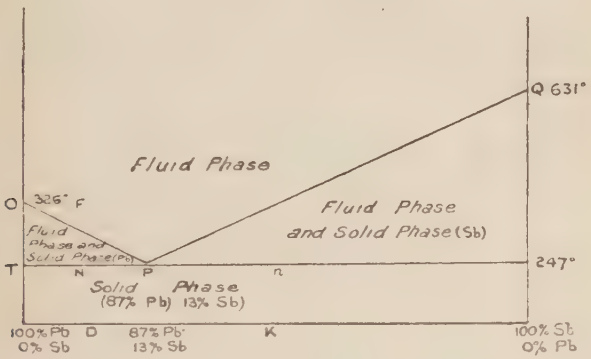



Fig. 23.—Freezing-Point Curve of Alloys of Lead and Antimony.

porphyritic crystals of lead in a ground mass consisting of the eutectic. Alloys containing more than 13 per cent. of antimony—as for example, at K—will deposit first excess of antimony, then, at the temperature 247° C., a mixture of antimony and lead in eutectic proportion. This will result in a mass containing porphyritic crystals of antimony in a ground mass of the eutectic.

[1] *Gosselin*, Bull. de la Soc. d'Encour., p. 1301, 1896; also *Stead*, Journ. Soc. Chem. Ind., p. 31, 1897; also *Charpy*, Metallographist, p. 87, 1898.

Finally, alloys containing 13 per cent. antimony will solidify completely at 247° C. to a eutectic conglomerate.

Advantage is taken of the principles illustrated above in the Pattinson process of desilverizing lead. Lead-silver alloys, containing less than 4 per cent. of silver, deposit at first pure lead on cooling, the mother liquor becoming proportionately richer in silver. If the rate of cooling is varied, important differences in the distribution of the solid phase follow. In the lead-antimony alloys, as shown above, the excess constituent, with regard to the eutectic composition, forms well-defined phenocrysts, embedded in a eutectic ground mass, forming a fine-grained conglomerate.

FIG. 24.—CRYSTALLIZATION OF LEAD-ANTIMONY ALLOYS.

If the crystallization is allowed to proceed very slowly without disturbance, the crystals of the first separation accumulate on the cooling surfaces, and the mother liquor is gradually forced to the inner portion of the mass (see Fig. 24). Thus the crystals of early consolidation become separated from the eutectic which solidifies in the final stage. This local separation of phenocrysts and ground mass, which is a kind of liquation, is more pronounced the larger the mass of the solution and the slower the rate of crystallization. It is also more marked as the concentration of the liquid deviates from that of the eutectic. Eutectic solutions obviously cannot show this phenomenon and its occurrence depends upon the relative propor

on of the excess component compared with the utectic proportion. In the case of alloys cooled with xtreme slowness, gravity also may exert an influence pon the separation, and the mother liquor, if heavier nan the first-formed crystals, may tend to accumulate n the lower part, or *vice versâ*. Thus, in a lead-ntimony alloy with about 20 per cent. antimony the pper part is often found to consist of a porphyritic nass of antimony phenocrysts, with very little ground nass; while the lower part is a uniform mass of utectic conglomerate, with few distinct crystals (see ig. 25).

Application to Fused Minerals. — Considerable nterest attaches to the experiments of Day and Shep-

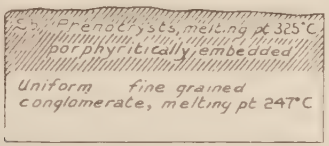



Fig. 25.—Crystallization of Lead-Antimony Alloy containing 20 per Cent. Antimony.

erd on the lime-silica series of minerals.[1] In this ase three eutectic points were found. The first ccurred at a temperature of 1417° C., when the con-entration of the melt was 63 per cent. silica and 37 per ent. lime, and the eutectic mixture consisted of tridy-nite and pseudo-wollastonite. The second eutectic oint occurred at 1430° C., when the concentration of he melt was 46 per cent. silica and 54 per cent. lime, vhen a mixture of pseudo-wollastonite and a form of me olivine was deposited. The third eutectic point ccurred at 2015° C., at a concentration of 32·5 per ent. silica and 67·5 per cent. lime, at which point lime livine and lime were formed. This is an important

[1] Amer. Journ. Sci., xxii. 265 *et seq.*, 1906.

confirmation of the view that fused silicates offer n exception to the laws governing aqueous solution and metallic alloys, although the conditions are ofte complicated by viscosity phenomena. The accon panying diagram (Fig. 26), given by Day and Shep

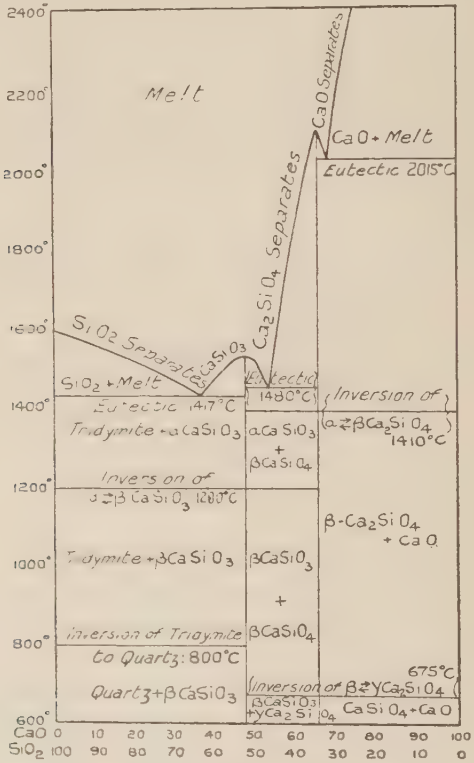



FIG. 26.—FUSION CURVE OF THE LIME-SILICA SERIES OF MINERAL (AFTER DAY AND SHEPHERD.)

herd, illustrates the above points, and shows, in add tion, the various transition temperatures at which t inversion of polymorphic forms took place.

The bearing of these phenomena upon magmas is the greatest interest, not only as illustrating a possib

explanation of a very common kind of differentiation, such as the acid streaks and cores of many eruptive rock masses, but also as bearing upon the phenomena of volcanic sequences. A suggestive example is afforded by the frequent reversal of phase which is noticed in a volcanic sequence—such, for example, as Harker has established in connection with the igneous rocks of Skye.[1] If it is remembered that the eutectic melts at a lower temperature than any other mixture, it is seen how a basic-acid sequence in one eruption may be followed by an acid-basic sequence in another, and *vice versâ*. It is only necessary to suppose that the abyssal rocks belonging to the earlier phase had during consolidation undergone a process of differentiation, as in the case of the lead-antimony alloys referred to above. On fusion of such a mass prior to the later period of vulcanism, the mass with the lower melting point would be the first to liquefy, and would furnish the earlier material for the ensuing eruptions. Barrow[2] has suggested a somewhat analogous explanation for the reversal of phase in the dyke stage. An eruption may begin with a refusion of an old magma, beginning with the lower part. Hence at first basic eruptions may precede acid eruptions. In the dyke stage consolidation had already begun at the top, and as the later dykes were fed from the still molten portions, these dykes would get gradually more basic as the material was derived from deeper parts. This explanation, however, assumes that the temperature of refusion coincides with that at which consolidation took place. This is improbable, because various vapour phases, such as water, may be no longer present. Although the consolidation point of a rock is lowered by the presence of the several con-

[1] *Harker*, Tertiary Igneous Rocks of Skye.
[2] Quart. Journ. Geol. Soc., xlviii. 120.

stituent minerals, it does not follow that the melting point of the solidified mass will also be lowered, for in a solid mass the solution laws do not apply until the minerals begin to melt.

Methods of Determining the Eutectic Composition. — The eutectic theory can be studied experimentally in the case of aqueous solutions by actual separation and weighing of the crystals which separate at different temperatures from solutions of various concentrations.

In the determination of the eutectic point of a binary alloy, also, it is easy to find the point of intersection of two fusion curves from the form of the cooling curve for different concentrations.

In the investigation of the cooling curves of fused silicates, however, there are many practical difficulties and these methods have been but little employed. Vogt has plotted fusion curves for some silicates of calcium and magnesium, which, in spite of some errors, show a close analogy with the theoretical direction required by the eutectic law.

Another and more direct method of determining the eutectic composition is to isolate the eutectic mixture and apply the method of quantitative analysis. Teall has adopted this plan in the case of the micropegmatite of the Stanner rock, and he thus found that the composition of micropegmatite approximates to 74·25 per cent. of felspar and 25·75 per cent. of quartz. Lagorio has proceeded in a similar manner to determine the chemical composition of the ground mass of certain rocks,[2] with the object of establishing the eutectic proportions of quartz and felspar.

Vogt has suggested a third way of arriving at this result. This consists in determining the limits of

[1] British Petrography, p. 402.
[2] Tschermak. Min. u. Pet. Mitt., viii. 173, 174, 1887.

formation of certain minerals and their sequence of separation.[1] Remembering that the excess constituent should, on the eutectic theory, separate first, and that a reversal of sequence should occur on either side of the eutectic composition, he has thus been led to the conclusion that the following are the eutectic proportions of certains pairs of minerals crystallizing from slags: Augite, 68 per cent.—olivine, 32 per cent.; augite, 40 per cent.—akermanite, 60 per cent.; fayalite, 75 to 80 per cent.—magnetite, 25 to 20 per cent.; melilite, 74 per cent.—olivine, 26 per cent.; melilite, 65 per cent.—anorthite, 35 per cent.; spinel, 2 to 3 per cent.—melilite + olivine, 97 to 98 per cent.

Vogt has discussed this question also from the point of view of Van 't Hoff's formula for the molecular depression of the freezing point. This formula is as follows:

$$\frac{dT}{da}\, m = 0{\cdot}0198\, \frac{T^2}{R},$$

where T is the melting point in absolute units, R is the latent heat of fusion, $m$ is the molecular weight.

The integration of this question presents difficulties, but by assuming the fusion curve to be a straight line—that is, by taking the tangent to the curve instead of the curve itself—the error will probably not be large, especially where the melting points of the two minerals do not differ by a large amount. We thus arrive at the linear equation:

$$t = 0{\cdot}0198\, \frac{T^2}{R}, \text{ or approximately } t = 0{\cdot}02\, \frac{T^2}{R}.$$

Thus, if we know the melting points of two minerals, as well as their latent heats of fusion and their molecular weights, we can plot the intersection of the two straight lines represented by the above equation; or

[1] Die Silikatschmelzlösungen, ii. 9-31.

the same result can be arrived at algebraically by solving simultaneously the two linear equations. This intersection will give the co-ordinates of the eutectic point.

It follows that the position of the eutectic point of two minerals is a mathematical function of their melting points, latent heats, molecular weights, and electrolytic dissociation.[1] Thus we have a definite relation between the eutectic point and the physical constants of two minerals. In the case of two minerals with widely different melting points, the eutectic point lies nearer to the mineral which has the lower melting point. Where the melting points are nearly the same the eutectic point will be nearly midway between them. It follows from this that every eutectic will have a smaller proportion of the more infusible constituent. The melting point has a far greater influence upon the position of the eutectic point than the other physical constants. The influence of latent heat will be in the same direction as the melting point, since minerals with a high melting point have also a high latent heat. Doelter, however, criticizes these conclusions.[2] He maintains that eutectic points cannot, in many cases, be determined by observation of the melting point. He affirms that the lowest softening point of glasses depends upon the concentration, and gives important information with regard to the eutectic composition. He maintains that superfusion renders untrustworthy the determination of eutectic points from either fusion curves or cooling curves, but that his experiments show that the curve representing the softening point of glasses of varying concentrations closely follows the cooling curve passing through the points at which crystallization begins. He further states that the

[1] Die Silikatschmelzlösungen, ii. 129 *et seq.*
[2] Sitz. d. K. Akad. d. Wiss., cxv. 628-744, 1906.

eutectic composition stage is marked by a small nterval between the first softening and the complete luidity of the glass, the eutectic behaving in this respect most nearly like a homogeneous substance. Further investigation of these points seems to be necessary.

Connection between Fusibility and Solubility.—The connection between the eutectic point and the melting point indicated above suggests a relation between the fusibility of minerals and their order of separation from magmas. It was once thought that the order of separation of minerals from a fused magma should be that of their relative fusibility, and even after the publication of the conclusions of Bunsen, Lagorio, Morozewicz, and others, to the effect that this order was determined rather by relative solubility, it was still often asserted that fusibility was the main factor in the sequence of crystallization. Thus Fouqué and Michel Lévy adopted this view in their great work on the synthesis of minerals and rocks, and still more recently Becke has asserted that the most infusible mineral usually forms the kernel of zoned crystals.[1]

In one sense the fusion point is a prime factor in the crystallization of a magma, since no mineral can separate at a temperature higher than its melting point. The fusion point gives, therefore, an upper limit of temperature at which crystallization is possible.

The fusibility and solubility of minerals are, however, connected in another way. The theory of eutectics demands that the excess component above the eutectic composition will separate first. The relation established above between the position of the eutectic point and the melting point shows that the most infusible mineral will generally be the excess constituent, since it forms the smaller proportion in the eutectic mixture.

[1] Tschermak. Min. u. Pet. Mitt., xvii. 97, 1897.

Thus fusibility and solubility are not necessarily two diametrically opposite standpoints, but are closely related to one another by the relative depression of the melting point.

The eutectic theory also furnishes an explanation why the normal order of increasing acidity, established by Rosenbusch, so often occurs in the sequence of crystallization of igneous rocks. The basic minerals have higher melting points, and are in most cases excess constituents in relation to the eutectic composition.

Reversal of the Normal Order.—Vogt has asserted as a general law that the sequence of crystallization is controlled by the rule that the mineral which is present in excess of the eutectic proportion is the first to separate from the solution. This theory explains certain problems of reversal of sequence in the order of crystallization. Thus, by varying the composition of certain slags Vogt succeeded in causing metasilicates to separate before olivine, or *vice versâ*. In basic rocks felspar may precede augite, or the latter may precede felspar. In the granites the relative order of separation of quartz and felspar is by no means constant. The normal order is reversed in the Eskdale granite, in which felspar plays the rôle of ground mass to the quartz.[1] Quartz often precedes orthoclase in the muscovite biotite granites, but it rarely does so in the biotite and hornblende granites. Again, both quartz and felspar occur as phenocrysts in many elvans.

Vogt's theory receives confirmation from many facts recorded in geological literature. Thus, in the main mass of the Shap granite quartz crystallized before the later generation of orthoclase, whereas in the basic secretions in the same rock quartz crystallized last. In the banded varieties of this rock some bands have

[1] *Teall*, British Petrography, p. 323.

abundant quartz, which then precedes the felspar, whereas in those bands in which felspars predominate these crystallized before the quartz.[1] Harker found that in the Isle of Rum either olivine or anorthite crystallized first, according to their relative abundance, from a simple binary magma containing anorthite and olivine, with an insignificant amount of augite.[2] A similar explanation may be given in cases where, as in some varieties of the granite of Rapakiwi, orthoclase precedes plagioclase.[3]

In the more complex magmas, however, a difficulty seems to arise in connection with the early separation of minerals which can scarcely be called excess constituents, on account of their small quantity. In rocks containing spinel, felspar, and a ferro-magnesian mineral, spinel separates first, even when only present to the extent of not more than 2 per cent. Similarly, the early separation of ilmenite, titanite, zircon, apatite, and other minerals, may be noticed even when these minerals are present in very small proportions. To these reference will be made later. Many anomalies in the sequence of crystallization may be due to superfusion and viscosity. Meyerhoffer[4] has illustrated this by means of the accompanying diagram (Fig. 27).

Cooling may proceed below the eutectic point E without crystallization taking place, owing to superfusion. There is then a possibility of four provinces, as shown in the figure. In Field II. the presence of a small crystal of A would cause A to crystallize, the composition of the magma changing towards the right until equilibrium is reached along the line SAE. Or the magma might cool without separation of A until the line EF was reached, when B might be the first

[1] *Harker* and *Marr*, Quart. Journ. Geol. Soc., xlvii. 275 *et seq.*
[2] Natural History of Igneous Rocks, p. 171.
[3] *Vogt*, Die Silikatschmelzlösungen, i. 156.
[4] Zeit. f. Kryst., xxxvi. 593 *et seq.*, 1902.

to crystallize. Thus either A or B might appear first in the same magma, according to the circumstances governing supersaturation. A reversal of the normal order, therefore, might occur if the supersaturation conditions of A and B are very different. Thus if the supersaturation of A is strong, while that of B is weak, then B may separate first even when the magma is supersaturated with A. Or, again, A may continue to separate below the eutectic point, the separation of B being checked by supersaturation. At length, at any

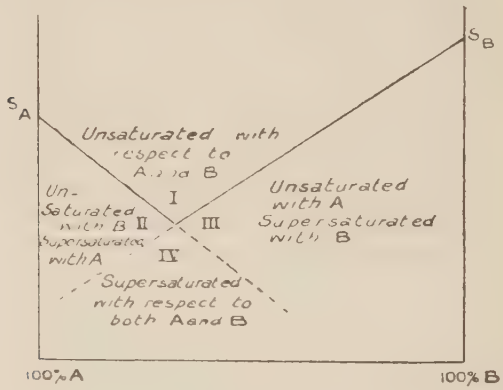



FIG. 27.—INFLUENCE OF SUPERSATURATION. (AFTER MEYERHOFFER.)

point, there may be a sudden separation of B, with a liberation of latent heat sufficient to check the further separation of A, and even to cause its partial resorption. It is only when the concentration of the magma gets back to the eutectic point that both A and B will separate together in eutectic proportions. This would explain not only many reversals of the normal order of separation, but also deviations from the eutectic proportions. For example, micropegmatite often frames the felspar phenocrysts in such a manner that the quartz increases in proportion in the outer margin of

he frame, thus giving a composition which does not orrespond with that of the true eutectic. Meyerhoffer as also pointed out that the velocity of crystallization may influence the result. One component may rystallize quickly and another quite gradually, the atter being displaced by its more rapidly growing ompanion. There may then occur a repetition of ach mineral in turn, owing to oscillatory conditions n the neighbourhood of the eutectic point, leading to condition which Vogt has suggested as a possible xplanation of certain concentric structures, such as

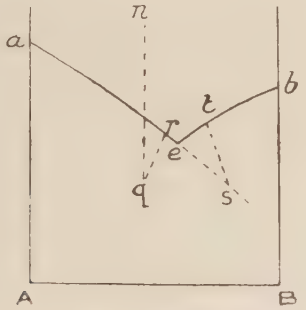



FIG. 28.—SHOWING THE INFLUENCE OF SUPERSATURATION ON THE ORDER OF CRYSTALLIZATION.

nose occurring in orbicular diorite.[1] Similar oscilatory conditions of equilibrium, according to Harker, re illustrated by the zoned felspars, consisting of lagioclase and orthoclase, in the large felspars of the apakiwi granite.[2]

The general conditions of oscillatory equilibrium re explained by the diagrams shown in Figs. 28 nd 29. In the first case (Fig. 28) a magma of composition, *n*, on cooling may become supersaturated at *q*, hen the mineral A crystallizes and the composition

[1] *Vogt*, Die Silikatschmelzlösungen, p. 137, footnote.
[2] Natural History of Igneous Rocks, p. 268.

changes along *qr*, until the saturation line *ae* is reached at *r*; A may continue to separate along *as* beyond the eutectic point *e*, when the magma is supersaturated with regard to B. At *s* the mineral B begins to separate and A is partially resorbed, the composition changing until the line *bt* is reached at *t*. B may then separate along *bte*, and on reaching *e* the two minerals separate together in eutectic proportions. In the case illustrated in the diagram (Fig. 29) a somewhat similar process takes place, but the mineral B separates first although the composition of the magma may be such

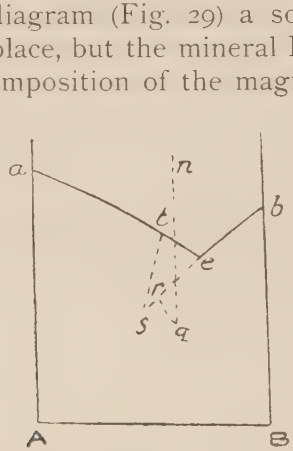



FIG. 29.—SHOWING THE INFLUENCE OF SUPERSATURATION ON THE ORDER OF CRYSTALLIZATION.

as to lead to the expectation that A would be the first to appear. Superfusion, therefore, may cause not only reversals in the order of crystallization, but also may result in a marked sequence of separation in place of the simultaneous crystallization of the eutectic.

These facts recall the experiments of Miers and Isaac upon the supersolubility curve (see *ante*, p. 60). The main separation of crystals may take place at the temperatures of the supersolubility curves, and on this account in general the mixtures may not solidify as eutectics; but either substance may, according to the conditions of supercooling, crystallize before the other

even in mixtures approaching the eutectic composition.[1] For this reason the hypertectic point—that is, the point of intersection of the supersolubility curves—may often be more important than the eutectic point.

The Eutectic Structure.—It has been urged as an objection to the eutectic theory of rock magmas that these comparatively seldom display any sign of a typical structure, such as has come to be associated with micrographic intergrowths of a nature resembling the laminated pearlite of the iron-carbon alloys. Laminated pearlite, however, is by no means the universal form displayed by the eutectic mixtures of ferrite and cementite. This is only characteristically shown in annealed steel.[2] An essential condition for its formation appears to be slow crystallization without disturbance. In other cases granular pearlite is produced. Similarly in rocks typical micropegmatite requires very exact conditions for its formation.

This structure is, however, not confined to quartz and felspar. Micrographic intergrowths in the case of felspar and diopside, felspar and ægerine, felspar and lepidomelane, felspar and hornblende, felspar and nepheline, felspar and sodalite, have been observed.[3] Allport,[4] also, noted such intergrowths of felspar and augite in the coarser parts of the Rowley basalt. Such micropegmatitic intergrowths, however, must be looked upon as a special form of eutectic structure.

The Ternary Eutectic. — When there are more than two constituents, we can no longer represent the equilibrium conditions by the diagrams already given. It is then necessary to deal with solid figures or with their projections upon a plane surface. In the first

[1] See *Miers*, paper read before the Mineralogical Society, January 29, 1907.
[2] *Jüptner*, Siderology, p. 119, 1902.
[3] *Brögger*, Zeit. f. Kryst, xvi. 148-159, 1890.
[4] See *Teall*, British Petrography, p. 212.

place, it may be remarked that in the case of magmas there will usually be at least three constituents. Binary eutectics will be confined generally to the final stages of consolidation. In Fig. 30, *a*, *b*, and *c* represent three components, which do not react chemically upon one another and do not form mix-crystals. The ordinates *a*A, *b*B, and *c*C represent the melting points of each constituent in the pure state. Instead of fusion curves,

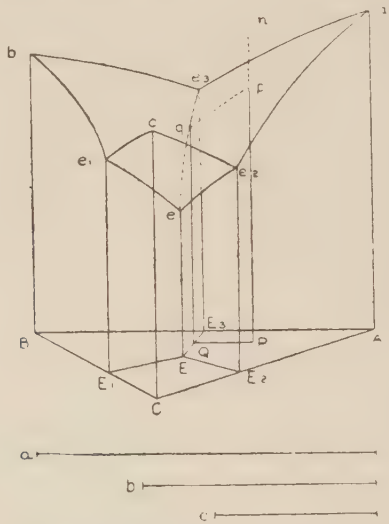



FIG. 30.—THE TERNARY EUTECTIC POINT, AND ITS PROJECTION UPON A PLANE TRIANGLE.

as in the case of binary mixtures, the fields $ae_2ee_3$, $be_1ee_3$, $ce_1ee_2$ represent fusion surfaces which meet in the point *e*. This point is a ternary eutectic point. These points may now be projected upon the horizontal plane ABC. The cooling conditions of a magma composed of three such substances may now be followed. Let the composition of the magma be represented by the point *n*, which may be called the figurative point. As cooling proceeds the fusion sur

face is met at the point *p*, and A begins to separate. The composition will now change along the line *pq* until at *q* both A and B will separate in constant proportions, the composition changing along the line *qe*. When the point *e* is reached, C begins to separate, and from this point onwards the three substances will consolidate together in eutectic proportions.

This course of events may be graphically shown by the three straight lines *a*, *b*, and *c* beneath the figure, where *a* represents the crystallization of A, *b* that of B, and *c* that of C. The whole sequence of changes may also be followed upon the plane triangle ABC, which being equilateral can be used to show any proportions of the three constituents by points within the figure.

Although the binary and ternary eutectic probably play some part in the consolidation of rock magmas, yet quaternary and even higher eutectics more often occur. These have scarcely yet been studied.

The observations above refer to magmas consisting of independent components — that is to say, those which do not form chemical compounds with one another, and do not form mix-crystals. It happens, however, that most of the rock-forming minerals are capable of forming mix-crystals to a greater or less degree. It is necessary, therefore, to examine how far the eutectic theory may apply to this class of substances.

# IX

## THE THEORY OF SOLID SOLUTIONS APPLIED TO GEOLOGICAL PROBLEMS

The Thermo-Dynamic Potential.—The general theory of equilibrium in the case of substances capable of forming mix-crystals is based upon thermo-dynamic principles, and involves a conception of what is termed "the thermo-dynamic potential." Potential may be defined as the capacity for doing work. It follows that the condition necessary for equilibrium is that the total thermo-dynamic potential should be a minimum. The value of the thermo-dynamic potential has, up to the present, only been determined in a few cases. It is obvious that the heat change of a reaction does not necessarily represent the whole change of energy. When, however, a reaction is accompanied by a change in volume, or by a change in electromotive force, we may measure the value of the thermo-dynamic potential by balancing these changes by an opposing pressure, or by an opposing electromotive force.

In the case of silicates the only extensive series of quantitative experiments bearing upon this point are those of Åkerman upon the total heat of fusion of various silicates and artificial slags.[1] Vogt has discussed the bearing of these results upon the depression of the melting points of mixed silicates.[2] For example

[1] Jernkontorets Annaler, 1886; also Stahl und Eisen, 1886.
[2] Die Silikatschmelzlösungen, ii. 31 *et seq.*

observing the total heat of fusion for different proportions of augite and olivine, that mixture which gives the lowest value for this factor is taken as the eutectic mixture of these minerals. This method, however, depends for its accuracy upon a correct determination of the melting point, and is not, therefore, easy to apply in the case of minerals which form mix-crystals, and therefore do not in general possess a sharp melting point.

Although the actual value of the thermo-dynamic potential may be unknown, we may express in a general way its application to the problems now under discussion by the graphic method proposed by van der Waals.[1] Thus, if we represent by abscissæ the number of gramme molecules of a solvent in which 1 gramme molecule of a solid is dissolved, and by ordinates the corresponding values of the thermo-dynamic potential, $\zeta$, for the liquid phase, we can then represent by a curve the changes in the value of the thermo-dynamic function at different concentrations. Suppose (Fig. 31) we start with a fused salt, and represent its thermo-dynamic potential by the point $a$ on the vertical axis. Let A represent the value of the thermo-dynamic potential for the solid substance. Now, the addition of successive small quantities of the solvent, represented by points along the $m$ axis, will cause the value of the thermo-dynamic potential to fall along a curve whose gradient is $\frac{d\zeta}{dm}$.

It can be shown that this curve at any point will be convex to the $m$ axis, and will have the form $a - log bm$. At infinite dilution it will become a straight line. Tangents to the curve at any points will cut the $\zeta$ axis in points equivalent to the value of $\zeta$ at the concentrations represented by the points on the curve. Thus

[1] Zeit. f. Phys. Chem., ii. 289, 1893.

at C the tangent meets this axis at A. But this poi represents the value of $\zeta$ for the solid phase; ther fore, at this concentration the solid and liquid phas are in equilibrium. At E the tangent cuts the ax below A, and, therefore, at this concentration th liquid phase is alone stable. Between *a* and C th potential of the liquid phase is greater than that of th solid; hence the liquid phase is unstable, and repr sents a supersaturated solution.

So far we have only considered variations in th concentration of the liquid phase. Suppose no

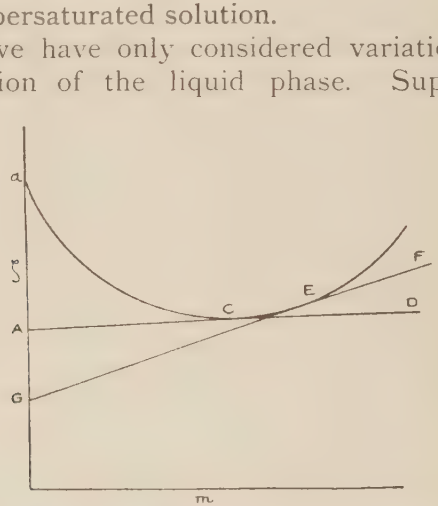



FIG. 31.—GRAPHIC REPRESENTATION OF THE THERMO-DYNAMIC FUNCTION. (AFTER RIJN VAN ALKEMADE.)

that the solid phase can vary. We shall then ha two curves in the diagram, one for the liquid a another for the solid. The possible results have be described in detail by Roozeboom.[1]

Although these curves represent the $\zeta$ functions, v may, for the sake of simplicity, look upon the cur for the liquid, called the "liquidus curve," as represe ing the temperature at which the solid begins to deposited from the solution. Similarly, the curve f

[1] Zeit. f. Phys. Chem., xxx. 385, 1899.

ne solid, called the "solidus curve," may be regarded as epresenting the temperature at which the solid begins o melt. As before, the abscissæ represent the rela- ve concentrations of the two substances A and B.

Mix-Crystal Series: Type I.—We will consider first the case n which A and B can form an nbroken series of mix-crystals, s in an isomorphous series.

At any temperature higher nan the melting points of A nd B the liquid phase must be table; hence the liquidus curve below the solidus curve, as the diagram (Fig. 32) in the pper section I. As the tem- erature falls we reach a point which the solid begins to eparate, and the two curves cut ne another, as in II. Drawing tangent at the points whose rdinates are *a* and *b*, it is seen nat *b* represents the composition the solid which is in equi- brium with a liquid of composi- on, *a*. At a still lower tem- erature, as in III., more of B eparates; while at a still lower mperature, represented in IV., e curves have changed places the solidus curve is entirely low the liquidus curve, and e solid phase is stable.

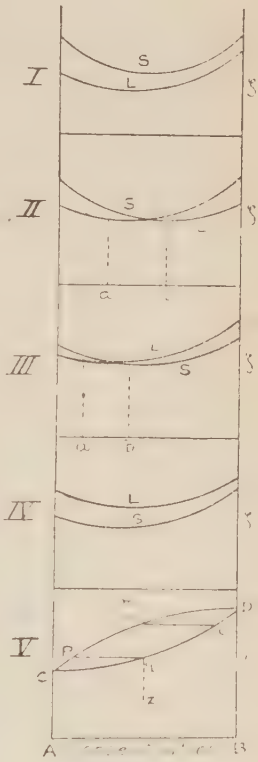



FIG. 32. — REPRESENTING SUCCESSIVE SECTIONS OF THERMO-DYNAMIC SURFACES. (AFTER ROOZEBOOM.)

These four diagrams represent successive sections a solid figure constructed on three axes, represent- g respectively the $\zeta$ function, concentration, and

temperature — viz., the thermo-dynamic surfaces o Gibbs. These sections are taken at right angles to the temperature axis. If a section of such a figure is taken at right angles to the $\zeta$ axis, we shall obtain a temperature-concentration diagram, in which $\zeta$ is constant. Such a diagram is shown in V. In this diagram C and D represent the melting points of the two pure substances, A, B, and the curves represent the equilibrium conditions, at each concentration, between the solid and liquid phases.

Thus, if we take any point *m* representing the concentration (see Fig. 32), on cooling, the upper curve is first reached at *n*. From *n* draw *no* parallel to AB to meet the solidus curve in *o*. It is then seen that a solid of composition represented by the ordinate through *o* is in equilibrium with a liquid of concentration represented by the ordinate through *n*. At a lower temperature the solidus curve is cut at *q*. Draw *qp* parallel to AB. It is then seen that a solid of composition *q* is in equilibrium with a liquid of composition *p*. Thus, between the temperatures represented by *n* and *q*, crystals of solid separate, varying regularly in composition from *o* to *q*, and at the same time the liquid has changed its composition from *n* to *p*. Below *q* the liquid solidifies completely to homogeneous mix-crystals, having the composition represented by the point *q*. We can thus trace the changes in the composition of the mix-crystals deposited during solidification of mixtures A and B in any proportion.

It should be noted that during the separation of the mix-crystals the liquid always contains more of that component by which the freezing point is depressed—*i.e.*, the component of lower melting point—and the separating crystals contain more of the component of higher melting point than does the liquid with

hich they are in equilibrium. This is important, nd shows that in this class of mix-crystals the first eparating crystals will have a larger proportion of e mineral with the higher melting point. This is possible explanation of Becke's observation that the ineral with the higher melting point generally forms e kernel of zoned crystals. Thus, in the case of oned olivine Becke found that the kernel consisted forsterite, while the outer zones were fayalite.[1]

For the complete realization of the conditions de-ribed above, it is, of course, necessary that cooling nould take place slowly to enable equilibrium to be stablished. The occurrence of regularly zoned rystals, therefore, affords some indication of the onditions under which consolidation took place. It also seen from the above considerations that iso-orphous mix-crystals of this type can have no sharp elting point, but have a melting point interval, which represented by the distance between the solidus nd liquidus curves—that is to say, by the difference etween the $\zeta$ functions for the solid and liquid phases. üster's rule[2] that the freezing point of all isomorphous ixtures lies on a line between the freezing points the pure components is not, therefore, rigorously xact, since the variation is not linear, but it is approxi-ately true when the interval between the two curves small.

Typical examples of isomorphous mix-crystal series this type are furnished by the forsterite-fayalite eries, the enstatite-amblystegite series, and by the bite-anorthite series. The latter has been recently udied by Day and Allen,[3] with the result that the pplicability of Roozeboom's explanation receives

[1] Tschermak. Min. u. Pet. Mitt., xvii. 97, 1897.
[2] Zeit. f. Phys. Chem., viii. 577, 1891.
[3] Amer. Journ. Sci., xix. 93, 1905.

strong confirmation. Pöschl has recently shown tha mixtures of diopside and hedenbergite from Elba als conform to this type.[1]

It is obvious that mix-crystal series of this type ca have no eutectic point, and the statement of Lane[2] tha the eutectic proportion of the triclinic felspars is repre sented approximately by $Ab_2An_3$ seems to have littl meaning.

Mix-Crystals: Type II.—The conditions represente above do not show all the possible ways in which th liquidus and solidus curves may cut one another in a unbroken mix-crystal series. The freezing-point curv

Fig. 33.—Mix-Crystals, in which the Freezing-Point Curve passes through a Maximum Point.

may pass through a maximum point, as in Fig. 33. I this case the freezing point of each component must b raised by the addition of the other component. At th maximum point the mix-crystal has the same compos tion as the liquid, and exhibits a sharp melting poi like a pure substance. Examples of this kind are rar and it is doubtful whether any have been recognize among the rock-forming minerals.

Mix-Crystals: Type III.—Another and a mo common case is that in which the freezing-point curv passes through a minimum (Fig. 34). This point mu not, however, be confused with a eutectic point. A

[1] Centr. f. Min., p. 571, 1906.
[2] Journ. Geol., ii. 83, 1904; also xii. 2, 82, 1903.

he minimum point only one homogeneous solid is leposited, and not a mixture of two solids, as at a inary eutectic point.

It is important to note the distinction which these atter types exhibit with regard to the order of separaion of the successive mix-crystals. In Type I. it was hown that the mineral with the highest melting point vill be concentrated in the earlier separation of the olid phase. In the case of Types II. and III. this order vill only hold in the right-hand portion of Type II., nd in the left-hand portion of Type III., or *vice versâ*. n the other portions of the curves the reverse order

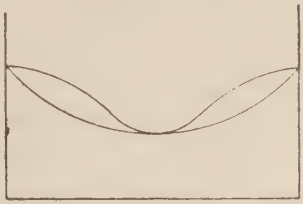



FIG. 34.—MIX-CRYSTALS, IN WHICH THE FREEZING-POINT CURVE PASSES THROUGH A MINIMUM POINT.

vill be followed; and zoned crystals are then possible vith a kernel having a lower melting point than the narginal part. The recognition of such a reversal in ne normal arrangement of zoned crystals would be ighly interesting, and would be a proof, as Vogt has lready pointed out,[1] that these would belong to one f these types, and not to Type I. It is obviously a ifficult matter to decide whether a given isomorphous ix-crystal series belongs to Type I. or to Types II. r III., and it is worth while to bear in mind the tatement of Roozeboom that the possibility of the urves exhibiting a maximum or a minimum point

[1] *Vogt*, Die Silikatschmelzlösungen, i. 150.

increases in proportion as the melting points of th pure minerals approximate to one another.[1]

A frequent occurrence in mix-crystals is a pronounce resorption of the inner zones.[2] A probable explanatio of this may be found in the fact that the solid whic first separates, as shown above, does not remain i equilibrium with the solution, which is continuall changing its concentration as crystallization proceed If, therefore, a crystal is not at once protected by fresh crystalline coating, it may readily undergo re sorption by the action of the magma. This will als explain the very common occurrence of irregula zoning exhibited by the pyroxenes in some dolerite Roozeboom's theory, in fact, shows that the zonin of mix-crystals is a phenomenon which would b expected to occur under conditions of constant pressur in a slowly cooling magma. It does not need an assumption of varying or recurrent changes in th conditions, but is a normal result of growth unde the changing equilibrium conditions prevailing durin the separation of mix-crystals. The greater the d vergence between the liquidus and solidus curves, th more pronounced will be the chemical difference between the adjacent zones.

Mix-Crystals: Type IV.—In this case the liquidu curve possesses a transition point, as shown at K i Fig. 35. The liquid phase at K is in equilibrium wit two different mix-crystals, having compositions corr sponding to the points D and E respectively.

An interesting example of this type seems to b afforded by the rhombic and monoclinic pyroxene and Vogt has suggested that this explains the con monly observed separation of rhombic pyroxene befo

[1] Zeit. f. Phys. Chem., p. 397, 1900.
[2] *Carveth*, Journ. Phys. Chem., ii.
[3] *Pöschl*, Centr. f. Min., p. 571, 1906.

nonoclinic pyroxene. As is seen in the diagram Fig. 35), when the MgO is largely in excess of CaO, nstatite is the first mineral to separate. The composi- on of the mix-crystals varies along AE, and com- aratively little CaO enters into their composition.

As the composition of the liquid changes along AK, he relative proportion of CaO in the liquid increases. At K a transition point is reached, at which the separa- ion of rhombic pyroxene ceases and that of monoclinic yroxene begins. Here two species of mix-crystal nay be produced—namely, rhombic pyroxene of omposition E, and monoclinic pyroxene of composi-

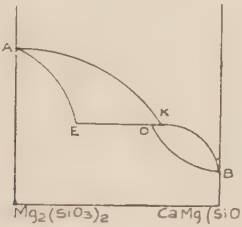



FIG. 35.—MIX-CRYSTALS, TYPE IV., IN WHICH THE LIQUIDUS CURVE PASSES THROUGH A TRANSITION POINT. (TYPE IV. OF ROOZEBOOM.)

on D. This would account for the intergrowths f rhombic and monoclinic pyroxenes occasionally ob- erved. Beyond this point only monoclinic pyroxene s deposited, and mix-crystals of the augite series, vith compositions changing along DB, are in equi- brium with liquids represented by corresponding oints on the curve KB. Thus $Mg_2(SiO_3)_2$ is con- entrated in the early separation, with a gradually ncreasing proportion of $Ca_2(SiO_3)_2$, until the point is reached, when the composition of the solution eaches the inversion point K, beyond which all the $Mg_2(SiO_3)_2$ enters into the augite mix-crystals.

While, therefore, only a little CaO enters the

enstatite series, a considerable amount of MgO enters into the augite series.

It follows from the above that the separation of iron-free enstatite after iron-free augite is theoretically impossible. The presence of iron materially alters the relative solubilities, and the reverse order may then be found to occur—that is to say, either hedenbergite or hypersthene can separate first. The system then belongs to another type.

Non-Continuous Mix-Crystals: Type V.—In the preceding types the components are completely

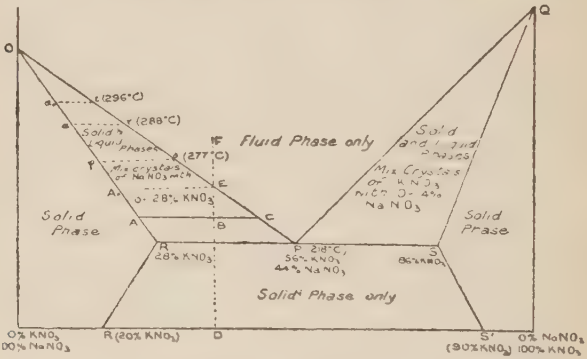



Fig. 36.—Mix-Crystals. (Type V. of Roozeboom.)

soluble in each other. They can, therefore, form an unbroken series of mix-crystals. Often, however, the pure substances are only soluble in each other to a limited extent. A case of this kind is exemplified by the nitrates of potassium and sodium, which have been studied by Carveth[1] and Hissink.[2]

The conditions of equilibrium are represented in the diagram (Fig. 36), the explanation of which is readily seen on following the process of cooling of a mixture of the salts fused together in any proportions.

[1] *Carveth*, Journ. Phys. Chem., ii.
[2] *Hissink*, Zeit. f. Phys. Chem., xxxii. 537, 1900

Assuming a concentration represented by any point D on the base line—namely, 34 per cent. $KNO_3$ and 66 per cent. $NaNO_3$—and cooling the mixture from the temperature denoted by F, when the line OP is reached crystals begin to separate. At a temperature of 240° C.—that is, at the point B—after equilibrium is attained, the crystals are separated and weighed. The ratio of the weight of the crystals to that of the mother liquor will then be found to correspond to the abscissæ of the points A and C; that is to say, crystals of the mixed nitrates, containing 21 per cent. $KNO_3$, are in equilibrium with mother liquor containing 42·5 per cent. $KNO_3$. The crystals are homogeneous mix-crystals. Wherever we take the point D between the limits of R and P, at the temperature of 240° C., we get the same mix-crystals with 21 per cent. $KNO_3$, and quantitatively

$$\frac{\text{Weight of mix-crystals}}{\text{Weight of mother liquor}} = \frac{BC}{AB}.$$

The nearer the point C, the smaller is the quantity of mix-crystals obtained, and at C no crystals separate—namely, BC = O. The nearer the point A, the larger is the quantity of separating crystals, and at A, where AB = O, there is no liquid phase, but the whole mass solidifies to homogeneous mix-crystals. Between A and C both solid and liquid phases exist in equilibrium. At other temperatures similar results may be obtained, and it is found that OR is the locus of all points to the left of P, at which only the solid phase exists at temperatures above 218° C., which is the eutectic temperature. It follows, also, that as crystallization proceeds the composition of both mix-crystals and mother liquor varies, and these continually increase in their percentage of $KNO_3$ as the temperature falls to that of the eutectic.

Precisely similar results follow to the right of P, the

mix-crystals and mother liquor increasing in their percentage of $NaNO_3$.

At P, the eutectic point, mix-crystals having compositions represented by R and S both separate together.

The diagram also shows how, by fractional crystallization, a partial separation of the components can be brought about, until the eutectic composition is reached. It is seen, also, that the temperature of complete liquefaction differs from the temperature of complete solidification (except at the eutectic point) by a definite interval.

It is probable that there are numerous examples of this type of fusion curve amongst rock-forming minerals, although few have been studied in any detail. A good example seems to be afforded by the rhodonite-hypersthene series, investigated by Vogt.[1] The most important example, however, is that of orthoclase and albite, as shown by Vogt. He supports this view by an examination of analyses by Lagorio and Holmquist, showing the composition of the felspars separating at different stages in the crystallization of igneous magmas. According to these results, it appears that the eutectic point is approximately at 40 per cent. orthoclase and 60 per cent. albite. If orthoclase is in excess of this ratio it should separate first, as in the case in the granite of Rapakiwi. Thus, orthoclase is zoned by plagioclase in the porphyrite of Canisp, and plagioclase is zoned by orthoclase in the trachyte of Mont Doré.[2]

Conditions for the Formation of Mix-Crystals.—The exact conditions which determine the formation of an unbroken mix-crystal series are somewhat obscure. Nernst has pointed out that the degree o

[1] Die Silikatschmelzlösungen, ii. 110.
[2] *Teall*, British Petrography, p. 298.

miscibility increases with the chemical analogy of the substances concerned. Thus, ammonium chloride and ferric chloride, which have very little chemical analogy, can only form mix-crystals in a very limited degree. Chemical analogy, however, is not alone a test of true isomorphism.[1] Neither is the power of forming zoned crystals, since crystals of monoclinic pyroxene can be zoned with rhombic pyroxene, and orthoclase can be zoned with plagioclase, and *vice versâ*. Retgers defines isomorphism as the property of those substances whose mix-crystals show additive properties, but this definition would exclude the forsterite-fayalite series, which cease to show additive properties in proportion as the iron percentage increases. Thaddéef has suggested as an explanation of this anomaly that $Fe_2SiO_4$ may be crypto-dimorphic, a polymerized denser modification entering into the olivine mix-crystal series.[2] In many cases the terminals of a mix-crystal series are not known in Nature in a pure state. Thus in the rhombic pyroxene series, although one terminal, enstatite, $MgSiO_3$, is known, the other terminal, $FeSiO_3$, is unknown.

It is not always possible, therefore, to apply the additive test satisfactorily to a mix-crystal series. The periodic variation, established by Tutton,[3] offers a promising field for the investigation of the properties of mix-crystals from a chemical point of view. Thus, the formation of a complete series between albite and anorthite, and not between triclinic potash felspar and anorthite, may be due to the fact that the atomic volumes of calcium and sodium are nearly identical, while the atomic volume of potassium is very much larger. This influence of molecular volume has been

[1] *Arzruni*, Physikalische Chemie der Krystalle, pp. 100-118.
[2] Zeit. f. Kryst., xxvi. 68, 1896.
[3] Proc. Roy. Inst., part 1, xvii. 136, 1903.

discussed by Prior.[1] It is interesting, in this connection, to note that potash felspar is believed to form a mix-crystal series with the barium felspar celsian.

Morphotropy.—Nevertheless, the majority of the mix-crystal series which have been investigated in petrography do form a morphotropic series; that is to say, the introduction of successive increments of another molecule into a crystal produces an additive effect upon the crystallographic constants.[2] A non-continuous series may, as Vogt suggests, result from the morphotropic influence of the added molecule. He formulates the general law that the less symmetry a molecule possesses, the greater is its morphotropic influence. A rhombic molecule, therefore, such as $MgFe(SiO_3)_2$, will be very sensitive to the addition of a monoclinic molecule, and still more to a triclinic molecule. Now, $Ca_2(SiO_3)_2$ is monoclinic, and enstatite or hypersthene can only take up a small proportion of this molecule without altering its crystalline shape to one of lower symmetry; while a monoclinic mineral can form mix-crystals with a considerable proportion of $Ca_2(SiO_3)_2$ without change of crystalline form.[3] In this connection, the transition point K in Type IV., referred to above, possesses great interest.

A similar example is furnished by bitter spar, $MgSO_4.7H_2O$, and ferrous sulphate, $FeSO_4.7H_2O$. Mix-crystals of these substances are rhombic if rich in the magnesia salt, and monoclinic if rich in the iron salt.

Retgers[4] explains these facts, not by morphotropy, but by the existence of metastable crypto-dimorphic forms. He assumes that the rhombic mix-crystals contain a metastable rhombic form of $FeSO_4$, while

[1] Min. Mag., p. 218, 1903.
[2] See *Brögger*, Zeit. f. Kryst., xvi., B, 1890: xviii., 1890.
[3] *Vogt*, Die Silikatschmelzlösungen, i. 38.
[4] Zeit. f. Phys. Chem., ii. 534, 1889.

the monoclinic crystals contain a metastable monoclinic form of $MgSO_4$. Similarly, it might be concluded that while the monoclinic form wollastonite is the stable form of $CaSiO_3$, there is also a metastable rhombic form which enters into the enstatite series, and a metastable triclinic form which enters into the rhodonite series. This view would require $CaSiO_3$ to be crypto-trimorphic.

Whether, therefore, limited miscibility and non-continuous mix-crystal series may be due to morphotropy or to crypto-dimorphism cannot yet be definitely stated. The question of crystal structure has recently been discussed by Barlow and Pope[1] upon the principle of close-packing of spheres of atomic influence, combined with the law of valency volumes; but the subject is too complex to explain adequately here.

Mix-Crystals in Ternary Systems.—As has been already stated, orthoclase and albite possess only a limited degree of miscibility, and therefore fall into Type V. Orthoclase crystals may contain as much as about 28 per cent. of plagioclase, and plagioclase may contain as much as about 12 per cent. of orthoclase. The proportion of the anorthite molecule which can be taken up in solution by orthoclase is not definitely known, and can only be conjectured from the relative position of its melting point. If we endeavour to represent these conditions upon a triangular diagram, as in Fig. 37, the points A, B and C will represent 100 parts of orthoclase, albite, and anorthite respectively. Then E will represent approximately the eutectic point of orthoclase and albite, while E' represents that of orthoclase and anorthite. Albite and anorthite, being completely miscible, have no eutectic point. Now, suppose a magma of composition *m*,

[1] Trans. Chem. Soc., 1906, 1907, and 1908.

from which felspar crystals of composition $p$ are separating. The composition of the magma gradually alters in consequence along the curve $mt$, to which $mp$ is a tangent. Meanwhile, the separating felspar crystals are changing in composition along the curve $pq$, during all which time the mix-crystals are taking up a small proportion of orthoclase. At $q$ the curve $pq$ is cut by the tangent $qt$ to the curve $pt$ at the point

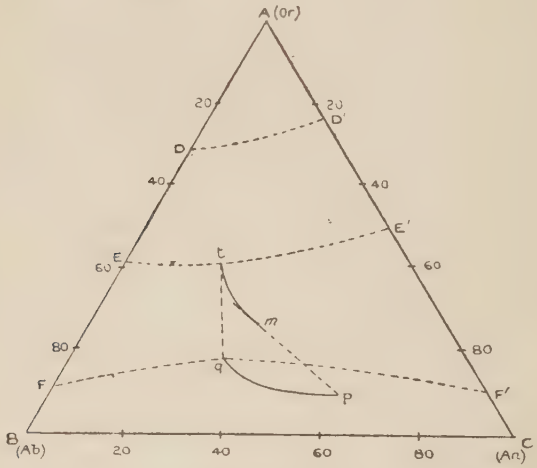



FIG. 37.

In the above diagram E represents the orthoclase-albite eutectic point, E′ represents the orthoclase-anorthite eutectic point; DD′ represents the limit of mix-crystals of orthoclase and plagioclase; FF′ represents the limit of mix-crystals of plagioclase and orthoclase. These limits are to a large extent hypothetical.

$t$ on the eutectic line EE′ of orthoclase and plagioclase. The point $q$, therefore, represents the limit of the proportion of the albite molecule that can enter into the plagioclase crystals. This explains the reason why pure albite is so rare a constituent of igneous rocks. The final residue of albite, instead of separating alone, is taken up by the orthoclase crystals. An objection was advanced by Fouqué against the plagio-

lase theory of Tschermak. Fouqué maintained that while anorthite often separates from magmas in a pure tate, albite does so but seldom.[1] It is seen, however, nat this may be a normal result of the variation of the omposition of the magma as crystallization proceeds. Becke has also remarked upon this point.[2] It now emains to consider the case of a ternary magma

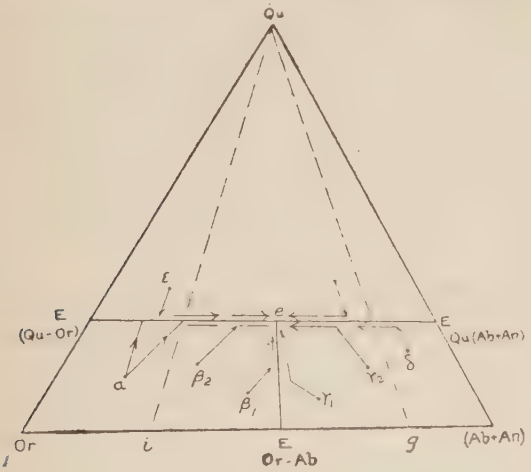



FIG. 38.

In the above diagram E and E (right and left) represent the eutectic points of quartz and orthoclase and plagioclase respectively; while E (at bottom) represents the eutectic point of orthoclase and plagioclase. *i* represents the limit of orthoclase-plagioclase mix-crystals; *g* represents the limit of plagioclase-orthoclase mix-crystals; *e* is the ternary eutectic point.

consisting of quartz, albite, and orthoclase. The composition of any such magma may be represented upon a triangular diagram, as in Fig. 38. By means of this diagram, the theoretical progress of crystallization of any magma composed of these three minerals may be followed. In the field in which is situated the letter *a*

1 Bull. de la Soc. fran. de Min., xvii., 1894.
2 See *Vogt*, Die Silikatschmelzlösungen, ii. 187.

the first to separate will be orthoclase mix-crystals, and if equilibrium is maintained during the separation of these crystals, the variation in the composition of the magma will be towards the vertex until the eutectic line EE is reached. Here orthoclase mix-crystals and quartz both separate together. Thus, from a ternary magma a binary eutectic may result.

In the same way, in the field in which is situated the point $\delta$ albite mix-crystals first separate, and finally a binary eutectic mixture of albite and quartz. If, however, equilibrium is not maintained during crystallization, the variation in the composition of the magma will follow the oblique arrows, becoming, in the first case, richer in albite, until finally the ternary eutectic point $\epsilon$ is reached, where quartz, orthoclase, and albite separate.

In a similar way we may follow the progress of crystallization in any of the other fields, the variation of the magma being shown by the arrows.

Generally, it follows from a consideration of this diagram that pure orthoclase should not separate from a magma which contains albite; neither should pure albite separate from a magma which contains orthoclase. The crystals of orthoclase, therefore, in rocks will often contain more or less albite dissolved in them, and those of albite will contain orthoclase in solid solution.

The diagram also explains why in many quartz-porphyries there are phenocrysts of quartz or of felspar, or of both of these minerals together, according to the field in which crystallization began and to the velocity of cooling. The simultaneous formation of both quartz and alkali felspar indicates that crystallization took place mainly in the neighbourhood of the eutectic line EE.

The presence of accessory minerals in the magma

will, to some extent, alter the conditions of consolidation, but the main features should generally be as described above. Thus the presence of anorthite will not disturb the conditions to a great extent, because of the complete solubility of albite in anorthite, or *vice versâ*.

Broken and Recurrent Series.—The progress of crystallization of minerals in a ternary magma may be conveniently represented by a series of parallel straight lines, as shown in Figs. 39, 40, and 41. Here the small letters *a*, *b*, and *c*, are used to denote the separation of pure substance, and the capital letters A, B, and C to denote the separation of mix-crystals. In the same way the thin lines denote the separation of two or more minerals together, while the thick lines denote the separation of one mineral alone. The shaded lines denote the recurrence of crystallization of a mineral which has been checked for a time. This graphic method may conveniently be used in conjunction with the triangular diagrams representing the changing composition of the magma.

Schreinemakers[1] has studied the conditions which may give rise to a continuous or broken sequence of crystallization. Consider first the diagram Fig. 39. The thick line *sv* is a fusion curve. The substances *b* and *c* form mix-crystals of Type V., their limits of miscibility being represented by the points $M_b$ and $M_c$. The arrows show the direction of falling temperature, and, therefore, the direction in which crystallization proceeds. The end crystallization takes place at *r* in whatever field we begin. It is to be noted that the point *v* is not a ternary eutectic point, since it has a higher temperature than *r*. Within the field *atvr* only the *a* substance separates; within the field *brvs* only the B mix-crystals separate; and within the field *csvt*

[1] *Schreinemakers*, Zeit. f. Phys. Chem., l. 169; li. 547; lii. 513.

only the mix-crystals C separate. Along the line *s* the mix-crystals B and C both separate. Along *t* pure substance *a* and mix-crystals C both separate Along the line *vr* pure substance *a* and mix-crystal B separate.

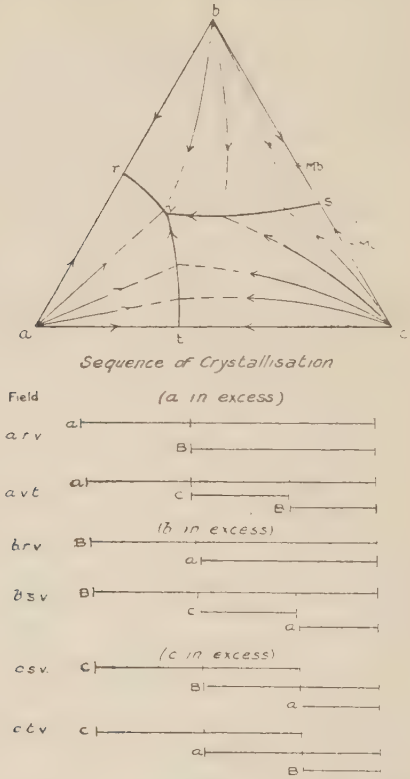



FIG. 39.—SEQUENCE OF CRYSTALLIZATION IN A TERNARY MAGMA. (AFTER SCHREINEMAKERS.)

The whole process of separation in any field represented graphically by the lines beneath th diagram. It is to be noted that in two fields, *arv* an *brv*, the substance C does not appear at all. Th resembles the case described above, where a binar

utectic of quartz and orthoclase, or quartz and albite, eparate from a ternary magma.

Another case is represented in Fig. 40. Here the urve *spv* is partly a fusion curve—namely, as far as the

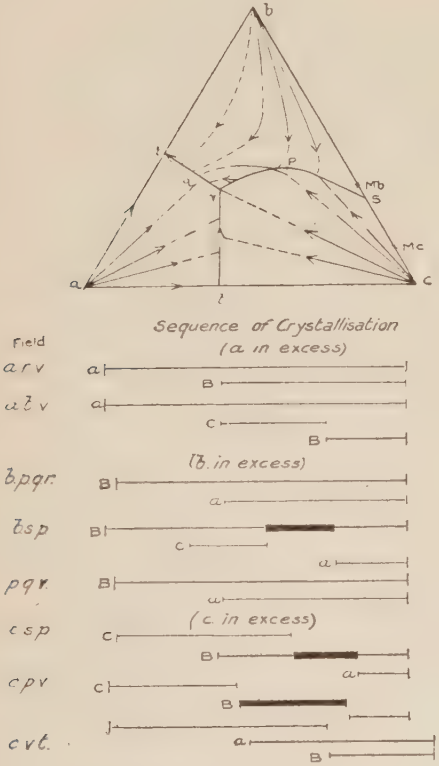



FIG. 40.—CRYSTALLIZATION IN A TERNARY MAGMA. (AFTER SCHREINEMAKERS.)

oint *p*; and partly a transition curve—namely, the part *v*. At every point in the curve *sp* mix-crystals of $M_b$ nd $M_c$ separate simultaneously, but in the portion *pv* nly $M_b$ separates. The curves from *c* pass over the ortion *pv*, and reach *vr* at a point *q*. Consequently

between $p$ and $q$ only B separates. In this case th
crystallization of C is excluded altogether in certai
fields, while B separates alone in others.

In Fig. 41 similar conditions arise, the only differenc

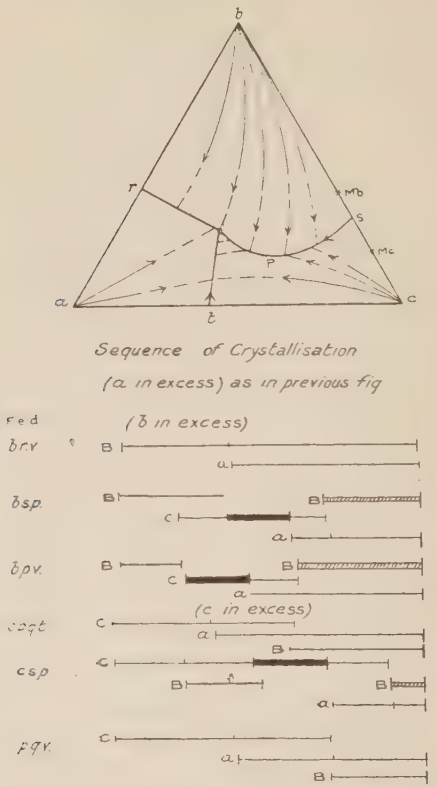



FIG. 41.—INTERRUPTED CRYSTALLIZATION IN A TERNARY MAGMA. (AFTER SCHREINEMAKERS.)

being that the curve *spv* is convex in the opposite dire
tion. The progress of consolidation may be follow
by means of the arrows, as in the other examples.
this case examples of recurrent crystallization arise
the B mix-crystals. Many other cases have been d

cussed by Schreinemakers in his paper referred to above.

Vogt applies the principle of interrupted crystallization to the case of the separation of enstatite and augite, where augite is the B mineral and enstatite is the C mineral in the above diagram.

Similar applications of the same principle are used to explain the phenomena often exhibited by the spinel group, in which the separation of pleonaste and picotite is terminated at an early stage, and at a later stage magnetite appears.[1]

Equilibrium Adjustments in Crystals on Cooling. —It is a well-known fact that the amount of carbon contained in solid solution in iron varies with the temperature, and that the excess separates on cooling in a form known as "temper carbon."

Other alloys also undergo marked changes of constitution at temperatures far below their melting points.[2]

Examples of changes in solid crystals have also been referred to in describing the transition of dimorphous minerals (see *ante*, p. 98 *et seq.*).

It remains to consider how far changes may take place in solid crystals as a consequence of adjustments of equilibrium on cooling in the case of solid solutions.

Continuous mix-crystal series, belonging to Types I., II., and III., consisting of substances completely miscible in all proportions, would not be expected to show any changes from this cause; for although the earlier stages of crystals of Type I. do not remain in equilibrium with the solution in contact with them as crystallization proceeds, and are liable to resorption unless they are protected by a new coating, it does not follow that these are unstable *per se*. Such crystals, there-

[1] *Vogt*, Tschermak. Min. u. Pet. Mitt., xxvii. 141-155.
[2] Heycock and Neville, Phil. Trans. (A), ccii. 1-69, 1903.

fore, may preserve their sharp boundaries in succes sive zones for an indefinite period.

It is otherwise, however, in the case of non-con tinuous mix-crystal series, in which there is only imperfect miscibility. The degree of miscibility de pends largely upon the temperature. For example the experiments of Carveth and Hissink, referred t above, show that at 218° C. sodium nitrate may contai 28 per cent. of potassium nitrate; but at 0° C. th former only takes up 20 per cent. of the latter salt A crystal of sodium nitrate, therefore, which solidifie at the higher temperature is unstable at the lowe temperature. It is then supersaturated with the potas sium salt, which may then separate in the form o inclusions. In some cases this separation may tak the form of regular intergrowths.

In this way may be explained many of the schille inclusions long ago regarded by Judd as of secondar origin.[1]

Petrography affords many examples of this nature Thus, inclusions of magnetite in olivine may be due t the separation of magnetite held in solid solution to limited extent in the olivine crystals. A similar vie may be taken of the inclusions of titanic oxide commo in pyroxene.[2]

With regard to perthitic intergrowths, some of thes may be of eutectic origin; but Vogt suggests that th microcline structure is due to the spontaneous chang of orthoclase holding in solution plagioclase, whic separates owing to diminished solubility as the crysta cool.[3] Similarly, monoclinic pyroxene at a high ten perature dissolves enstatite, which separates in pe thitic fashion on cooling.

[1] *Judd*, Quart. Journ. Geol. Soc., xli. 374-389, 1885.
[2] *Vogt*, Quart. Journ. Geol. Soc., lxv. 101, 1909.
[3] Tschermak. Min. u. Pet. Mitt., xxiv. 537-541.

Perhaps other inclusions may be attributed to the ame cause. The vermicular quartz (" quartz de corro- ion " of Lacroix), common in the felspars of some granitic rocks, has been ascribed to the secondary eparation of silica from solid solution in felspar, in vhich its solubility decreases as the temperature falls, but there is no experimental evidence for such a con- clusion.

# X

## ON THE CONDITIONS OF CHEMICAL EQUILIBRIUM IN GEOLOGY

Modern chemistry rests mainly upon thermo-dynamical foundations, and is controlled by the laws of conservation of mass and of energy.

Allotropic forms of the same substance have different amounts of intrinsic energy. The form which possesses the largest amount of energy is the least stable. In general, the amorphous form of minerals possesses more energy than the crystalline form, and is less stable.

Similarly, those crystalline forms which possess a high degree of symmetry often possess less energy, and are more stable than those of lower symmetry. A high specific gravity, also, is often accompanied by smaller potential energy and greater stability. These rules, however, are not invariable, for calcite has a lower specific gravity, although higher symmetry than aragonite, and is more stable. Cyanite has a higher specific gravity and a lower symmetry than andalusite or sillimanite, and is more stable than these.

In speaking of the relative stability of allotropic forms, however, it is necessary to define the conditions of temperature and pressure. As has been already shown, allotropic forms possess a definite transition point. At the transition point we may have a reversible cycle, where the change can proceed in either direction. At this point what is known as the Carnot-

Clausius principle obtains—*i.e.*, the entropy change s zero. This is usually expressed by the relation $\Sigma\frac{Q}{T} = O$, where Q is the heat change and T is the abso-

ute temperature. Hence, when a reversible change is carried out at constant temperature, $\Sigma Q = O$, or the sum of the heat changes is zero, and no heat passes into any other form of energy, such as work. It follows hat the work accomplished is also zero. Hence, at he transition point the intrinsic energy of each allo-ropic form is the same. Above or below this point one or the other form will possess more energy than he other, and will be less stable. It is thus possible o predict the direction in which change can take place.

The principle of maximum work shows that where ny change can accomplish work in overcoming re-istance, that change will take place when the resistance s absent. The possibility of doing work, therefore, etermines the possibility of every chemical reaction.

Capacity for doing work may be measured in practice ither by the heat effect, or by the volume change, or y the development of electromotive force.

Stability, therefore, may be defined as the absence f capacity for doing work.

Reversible Reactions.—In the case of ordinary hemical reactions, when the products of the reaction re not removed, the reaction is probably never com-lete, but at a certain stage reaches an equilibrium oint, at which it can proceed indifferently in either irection.

This reversibility of chemical reactions at the equi-brium point is not always apparent at ordinary emperatures. Van 't Hoff illustrates this by the xample of a ball without inertia rolling on a smooth urve. In the diagram (Fig. 42) GH represents the ase in which the reaction is apparently complete.

This means that the ball stops at an equilibrium point so near H that it is indistinguishable from it. In reality, however, the completeness of the reaction is only apparent, and at higher temperatures the equilibrium point is usually displaced towards the left, and the reversibility of the process can be recognized. An example of this is afforded by the union of oxygen and hydrogen, which at the temperature of the oxy-hydrogen flame is a reversible reaction, with a definite equilibrium point. In other cases the equilibrium point is well marked even at ordinary temperatures, the case

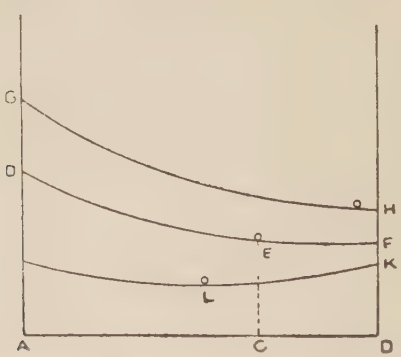



FIG. 42.—ILLUSTRATING CHEMICAL EQUILIBRIUM AND REVERSIBILITY OF CHEMICAL REACTIONS. (AFTER VAN 'T HOFF.)

being then represented by E on the curve DF. The heat effect in the first kind of reaction is always large The smaller the heat effect becomes, the more the equilibrium point is displaced towards the left on raising the temperature, until when the heat effect is zero it lies exactly in the middle, as at L on the curve IK. Examples of this kind of reaction are afforded by some stereoisomers, in which the two transition forms have identical molecules, but these are differently arranged. Possibly right- and left-handed quartz may also belong to this type.

The reason why the equilibrium point is usually displaced towards the left at higher temperatures is explained by Van 't Hoff's law of mobile equilibrium. When the direct reaction is exothermic, the reverse action is endothermic. A rise in temperature disturbs the equilibrium point in the direction which results in the absorption of heat. For this reason, exothermic reactions will not proceed so far at a high temperature as at a low temperature. At a high temperature the reverse action is accelerated, and the equilibrium point moves backwards. Most chemical reactions, therefore, are what may be called balanced actions. For example, the action of heat upon calcium carbonate is represented by the reversible equation—

$$CaCO_3 \rightleftharpoons CaO + CO_2.$$

The reaction towards the right only proceeds so long as the dissociation tension of the calcium carbonate exceeds the vapour pressure of the carbon dioxide present in the system. It can only be made complete by withdrawing the carbon dioxide from the sphere of action. Similar phenomena occur in the dehydration of natural hydrates, as already explained.

The principle of reversibility explains a large number of cases in which ordinary laboratory reactions are apparently reversed in natural processes. Many such cases may be recognized in the study of pseudomorphs. Thus, pseudomorphs of pyromorphite occur in the form of galena, and pseudomorphs of galena in the form of pyromorphite. The principle of reversibility must, however, be applied with caution in geological chemistry. In a thermo-dynamical sense reversibility requires that the process can be reversed at the equilibrium point by an infinitesimal external change in the conditions. The process, however, requires time, and may be delayed by viscosity and other causes. In the case of

such retardation it is a matter of considerable difficulty to maintain exact equilibrium for a length of time sufficient to insure the result. This is particularly the case in geological processes, owing to the continual variation in the concentration of the reacting substances, as well as in the temperature and pressure of the environment. But, although exact reversibility may be thus prevented, the processes are reversible. Van Hise concludes, probably correctly, that reversibility is a general law in the two regions of the earth's crust, which he calls the zone of anamorphism and the zone of katamorphism.[1] Thus oxidation and deoxidation, hydration and dehydration, carbonation and silication, are processes reversible under different conditions of temperature, pressure, and concentration. Examples of this are very numerous. As an illustration may be mentioned the alteration of albite into analcime, which may be represented reversibly thus:

$$Na_2O.Al_2O_3(SiO_2)_6 + 2H_2O \rightleftarrows Na_2O.Al_2O_3(SiO_2)_4.2H_2O + 2SiO_2.$$

Similarly, it is known that enstatite and olivine pass into serpentine, whereas serpentine on fusion splits up into enstatite and olivine; the reaction is, therefore, reversible as in the equation[2]—

$$2H_2O.3MgO(SiO_2)_2 \rightleftarrows MgSiO_3 + Mg_2SiO_4 + 2H_2O.$$

Other examples of reversible reactions may possibly be afforded by the reaction of olivine and anorthite forming augite, thus:

$$CaO.Al_2O_3(SiO_2)_2 + Mg_2SiO_4 \rightleftarrows (MgO.Al_2O_3)\ (CaO.MgO[SiO_2]_3).$$

In the same way anorthite and forsterite can perhaps transform reversibly into spinel and diopside, thus:

$$CaO.Al_2O_3(SiO_2)_2 + Mg_2SiO_4 \rightleftarrows MgO.Al_2O_3 + CaO.MgO(SiO_2)_2 + SiO_2.$$

[1] *Van Hise*, Treatise on Metamorphism, pp. 366, 367, 1905.
[2] *Daubrée*, Comptes Rendus, lxii. 661, 1866.

It is possible, also, that there may be a reversible reaction between albite and nepheline, as below:

$$Na_2O.Al_2O_3(SiO_2)_6 \rightleftharpoons Na_2O.Al_2O_3(SiO_2)_2 + 4SiO_2,$$

and between leucite and orthoclase and potash nepheline, thus:

$$2(K_2O.Al_2O_3[SiO_2]_4) \rightleftharpoons K_2O.Al_2O_3(SiO_2)_6 + K_2O.Al_2O_3(SiO_2).$$

In the latter case, since leucite is the more stable form at high temperatures, the reaction would proceed from right to left under these conditions, and would thus explain why leucite is more common in rocks of volcanic origin.

Mass Action.—If we consider an ordinary case of double decomposition, such as the reaction at the temperature of boiling water between barium sulphate and sodium carbonate, we have the reversible reaction

$$BaSO_4 + Na_2CO_3 \rightleftharpoons BaCO_3 + Na_2SO_4.$$

An equilibrium is established in this case when the concentration of the $Na_2CO_3$ is five times that of the $BaSO_4$. At this concentration the reverse action exactly balances the direct action. At a greater concentration the reaction proceeds towards the right, and $BaSO_4$ is decomposed; at a less concentration the reaction proceeds towards the left, and $BaCO_3$ is decomposed. Thus, in a solution containing these salts either heavy spar or witherite can be deposited, according to the relative masses present.

A further example will illustrate this more clearly. Berthollet explained the presence of trona ($Na_2CO_3.NaHCO_3.2H_2O$) on the shores of the natron lakes of Egypt by the decomposition of sodium chloride by calcium carbonate.[1] This assumes the reversibility of the ordinary laboratory reaction:

$$CaCl_2 + Na_2CO_3 \rightleftharpoons CaCO_3 + 2NaCl.$$

[1] Ann. de Chim., xxxvi. 302, 1801; xxxvii. 225, 1801; xxxviii. 113.

Although we now know that trona, gay-lussite, and thermonatrite are more probably products resulting from the drying up of calcareous solutions, as illustrated in Van 't Hoff's researches on the Stassfurt salts, yet this early recognition of the principle of reversibility in geological chemistry is highly interesting.

Wenzel had previously called attention to the disturbing influence of the quantity of the reacting substance upon the direction in which chemical transformations proceed.[1] To these two earlier observers, therefore, is due the conception that chemical action is regulated, not only by the so-called affinity, but by the relative masses of the reacting substances, and that chemical reactions do not always proceed in one direction, but may be reversed by changing the relative masses of the reacting bodies.

At a later date Rose drew attention to many other examples of this kind,[2] pointing out that silicate rocks, although unaffected by the most powerful acids in laboratory experiments, yet weather readily in Nature under the comparatively feeble influence of water and carbonic acid. This decomposition of silicates in Nature affords a typical example of the principle of mass action.

The active mass is measured, according to the modern theory of ionic dissociation, not by the molecular concentration, but by the concentration of the ions. Molecules, as such, are believed to possess little or no chemical activity. Upon this view chemical activity largely depends upon the ionizing power of the solvent. In geological processes the influence of water in this respect is great, because owing to its high dielectric constant, it possesses a

[1] See *Mellor*, Chemical Statics and Dynamics, p. 5, 1904.

[2] Pogg. Ann., lv. 415, 1842; lxxxii. 545, 1851; xciv. 481, 1855; xcv. 92, 426.

arge dissociating power. It is to the ions, therefore, hat all chemical reactions are believed to be due.[1]

In this connection it is important to remember that n geological chemistry dilute solutions play an im- portant part. Now, dilute solutions of electrolytes are most completely dissociated into ions, and are, herefore, relatively more active than strong solutions.

This hypothesis certainly explains why water plays so important a part in geological chemistry. Many of he most pronounced chemical reactions are found to cease in the absence of an ionizing substance. Thus, dry ammonia does not react with dry hydrochloric acid, and perfectly dry ammonium chloride does not dissociate by heat.[2] Dry hydrochloric acid, or dry sulphuric acid, has no action upon dry litmus, nor does dry hydrochloric acid have any appreciable effect upon carbonates.[3]

There are many other examples of a similar kind,[4] and the question arises whether in deep-seated plutonic regions, where the temperature is perhaps high enough to dissociate completely any water vapour that may be present, the chemical activities as they are known at the surface of the earth may not be com- pletely altered in character.

The Solubility Product.—In every solution the number of free ions will depend upon their relative rates of dissociation and recombination. Thus, if ionization take place twice as fast as recombination, two-thirds of the molecules present will be split up into ions. For every temperature and concentration there will exist a balance, which is determined by the

[1] Kahlenberg has attempted to show that this statement need not be universally true, and that instantaneous chemical reactions may take place in solutions which are not ionized (see Journ. Phys. Chem., vi. 1, 1902).

[2] Journ. Chem. Soc., lxv. 611, 1894.

[3] Phil. Mag., xxxiv. 117, 1892.

[4] *Perman*, Chem. News, p. 197, 1903; also Brit. Assoc. Rep., 1903.

equation $cc' = k\mathrm{C}$, where $cc'$ represents the concentrations of the ions and C that of the molecules.

The expression $k\mathrm{C}$ is called the solubility product. The ratio of the concentration of the ions to that of the molecules is constant—viz.:

$$\frac{c\,c'}{\mathrm{C}} = k.$$

Hence, a precipitate can only form by the reaction of salts in solution when the product of the ionic concentrations exceeds the solubility product.

Applying this principle, it is easy to see why excess of a soluble carbonate will alter celestine to strontianite, and excess of soluble sulphate will alter strontianite to celestine. The reversible equation is as follows:

$$\mathrm{SrSO_4} + \mathrm{Na_2CO_3} \rightleftharpoons \mathrm{SrCO_3} + \mathrm{Na_2SO_4}.$$

The direct reaction proceeds when the product of the ions on the left exceeds the solubility product of $\mathrm{SrCO_3}$. The reverse action takes place when the product of the ions on the right exceeds the solubility product of $\mathrm{SrSO_4}$. At any given temperature these reactions are balanced when the two solutions of strontium salt are in the proportion of their solubilities at that temperature. It follows that the more soluble one salt is in proportion to another, the more readily it can be altered by it. Thus, celestine, being more soluble in water than strontianite, is altered by a smaller proportion of carbonate than the amount of sulphate required to effect the reverse change, since for equilibrium conditions a solution of these salts will contain more strontium sulphate than strontium carbonate.

Exactly the reverse holds for heavy spar, $\mathrm{BaSO_4}$, as has been shown above. In the case of calcium sulphate the difference in solubility between $\mathrm{CaSO_4}$ and

$CaCO_3$ is so large that anhydrite or gypsum is readily converted into carbonate, but the latter is only very rarely altered into sulphate.[1]

Similar reversible processes probably explain the alteration of calcite and magnesite into the corresponding silicates. In all cases the general law holds good that the most insoluble mineral tends to separate from dilute solutions.

These principles control the many reactions characteristic of rock weathering. Such cases are particularly suitable for the illustration of the law of mass action, because weathering is generally the result of the reaction of dilute solutions.

In the case of strong solutions the problem is more complex, possibly owing to the mutual action between the parts of the dissolved substances, bringing into play attractions and repulsions, not only between the ions, but between them and neutral molecules.[2] The result may also be complicated, especially in the case of silicates, by the formation of complex ions.

Ionic Dissociation of Fused Silicates.—Beyond the fact that fused silicates conduct electricity, and are therefore presumably dissociated to some extent into their respective ions, very little is known of the dissociation of this class of matter. The experiments of Barus and Iddings upon the electric conductivity of fused silicates gave no further result than that the conductivity increases rapidly as the temperature rises. They also investigated the conductivity of magmas of different kinds, and their results seem to show that the conductivity increases with the acidity of the magma.[3] From this it may, perhaps, be inferred that the alkaline silicates, such as orthoclase and albite,

[1] *Ostwald*, Die Wiss. Grundlage der Analyt. Chem., p. 117.
[2] Zeit. f. Phys. Chem., xxxvii. 490-503, 1901; xli. 257-301, 1902.
[3] Amer. Journ. Sci., xliv. 242, 1892.

are more strongly dissociated than basic minerals, such as olivine, augite, anorthite, etc. Doelter[1] has pointed out that this agrees with the fact, supported by experiment, that basic minerals separate more readily from fusion in slags than do the alkaline silicates. Pure silica, on the other hand, is but little dissociated and possesses, therefore, great electrical resistance. Since dissociation into ions is facilitated by the presence of a substance possessing a high dielectric constant, it is possible that this part is played by silica and the higher conductivity of acid magmas may be thus explained.

Foussereau's[2] experiments point to a connection between electric conductivity and viscosity. He attempted to establish this relationship, and concluded that the conductivity of any salt at different temperatures is proportional to the viscosity—a result to be expected from the influence of viscosity upon the mobility of the ions. Doelter suggests that this may help to explain the small capacity for crystallization exhibited by the more viscous silicates. Owing to the feeble mobility of the ions near the freezing point of this class of substances, ionic equilibrium is not readily established. The substance remains dissociated, and crystals cannot form. This conforms to Roozeboom's theory that with substances possessing a sharp melting point ionization equilibrium is quickly established.[3] This same cause may influence the fusion curves, and prevent the appearance of a sharp eutectic point in cases where the viscosity is great. Viscosity thus establishes conditions of false equilibrium, and may explain the statement of Doelter[4] that the presence of the highly viscous mineral ortho

[1] Physikalisch-Chemische Mineralogie, p. 102.
[2] Ann. de Chim. et de Phys., vi. 5, 1885.
[3] Zeit. f. Phys. Chem., liii. 449, 1905.
[4] *Doelter, op. cit.*, p. 647.

clase raises the fusion point of a mixture of olivine and diopside, instead of lowering it, as Nernst's theory demands.

Influence of the Common Ion.—If we consider the case of the ionization of a solution of a simple salt, such as sodium chloride, in dilute solution, when ionization is complete, we get the equation—

$$NaCl = \overset{+}{Na} + \bar{Cl}.$$

In a stronger solution, at any given temperature, we have finally an equilibrium established between the ionized and unionized parts—that is,

$$NaCl \rightleftharpoons \overset{+}{Na} + \bar{Cl}.$$

Now, by what has gone before, it is known that the product of the concentrations of the ions is equal to the constant $k$ multiplied by the concentration of the unionized part—that is,

$$C^{+}_{Na} \cdot C_{\bar{Cl}} = k\, C_{NaCl} = k',$$

since in a saturated solution the concentration of the unionized part is constant.

Suppose hydrochloric acid is now added. This will give to the solution more $\bar{Cl}$ ions—that is, we increase the value of the factor $C_{\bar{Cl}}$. But since $C^{+}_{Na} \cdot C_{\bar{Cl}}$ must be constant, in proportion as $C_{\bar{Cl}}$ increases, $C^{+}_{Na}$ must diminish. Some Na ions, therefore, must recombine with Cl ions to form NaCl. Since, however, the solution is already saturated, this NaCl must separate in a solid form. Hence the addition of hydrochloric acid will determine the separation of some NaCl from a saturated solution of salt.

This result may be expressed generally by the statement that the addition to the solution of an electrolyte of a solution containing an ion common to it and the electrolyte will, in general, lower the

solubility of that electrolyte.[1] The converse of this law is important—*i.e.*, the solubility of one salt may be increased by the presence of another salt not containing a common ion. Thus, gypsum is slightly soluble in pure water, but it dissolves freely in the presence of NaCl.[2] Hence, large quantities of calcium sulphate can be taken up by natural waters containing sodium chloride in solution. Treadwell and Reuter have shown that the increase of solubility of calcium carbonate in similar circumstances is not so marked unless the sodium chloride is present in considerable amount,[3] possibly on account of the more feeble ionization of carbonates.

Again, the influence of the common ion may explain how limestone may be changed into either spathic iron or dolomite by contact with a solution of $FeCO_3$ or $MgCO_3$.

Vogt has utilized the theory of the common ion to explain certain phenomena in the crystallization of igneous magmas. The conclusions, however, involve assumptions respecting the ionization of magmas for which there is not absolute proof. For example, in the case of a magma containing spinel, $MgO.Al_2O_3$, and potash felspar, $K_2O.Al_2O_3(SiO_2)_6$, he assumes that the spinel molecule is dissociated into the ions $\overset{=}{Mg}$ and $\bar{Al}_2O_4$, and that the felspar molecule is dissociated into $\overset{+}{K}$, $\overset{+}{Al}$ and $\bar{Si}_3\bar{O}_8$ with no common ion. The felspar, therefore, will probably separate first from a magma containing, say, 95 per cent. felspar and 5 per cent. spinel, since the eutectic mixture is assumed by him to contain about 90 per cent. felspar and 10 per cent. spinel. But if a ferro-magnesian mineral is also present, this will furnish $\overset{+}{Mg}$ ions

[1] *Nernst*, Theoretical Chemistry, p. 446, 1895.
[2] *Cameron*, Sixty-fourth Report U.S. Dep. Agric., pp. 150, 151, 1900.
[3] Zeit. f. Anorg. Chem., xvii. 170, 1898.

which will lower the solubility of the spinel, and that mineral may then separate first, even when the magma only contains 2 per cent. of spinel. He suggests a similar explanation for the early separation of perowskite, titanite, ilmenite, iron glance, zircon, and apatite, even when these minerals are present in very small amount. On the other hand, quartz separates first only when the magma is very rich in silica, because $SiO_2$ is not appreciably dissociated into ions.

Similarly, olivine separates first, even when present in comparatively small proportions, owing, in his opinion, to the lowering of its solubility by the common $\overset{+}{Mg}$ ion furnished by other ferro-magnesian silicates. It is only when olivine is present in very small proportions that other silicates precede it in separation.

Vogt, in fact, adduces the theory of the common ion to explain many cases in which the order of separation appears to differ from that demanded by the eutectic theory.[1] Harker shows that this theory is supported by the phenomena observed in the Isle of Rum, where, in the ultrabasic rocks, olivine and anorthite usually crystallize in accordance with their relative proportions with respect to the eutectic composition; but if pyroxene is present in considerable amount, the olivine always crystallizes first.[2]

It is obvious that the presence of a common ion will alter the eutectic composition. It displaces the eutectic point in a direction away from the mineral which has the higher melting point, and accentuates the separation of minerals in the inverse order of their fusibility.

If we examine the theory of the common ion closely, it becomes evident that considerable caution must be

[1] *Vogt*, Silikatschmelzlösungen, ii. 151-156, 1904.
[2] *Harker*, Natural History of Igneous Rocks, pp. 204, 205.

observed in its application. For example, the solubility of lead sulphide in water is reduced by the addition of a weak solution of sulphuric acid, and the solubility of silver chloride is reduced by the addition of a weak solution of hydrochloric acid; but strong sulphuric acid increases the solubility of lead sulphate, and strong hydrochloric acid very considerably increases the solubility of silver chloride. Similarly, the ammonium-magnesium phosphate precipitate is more soluble in strong ammonia solution than in pure water. Again, iodine is more soluble in solution of potassium iodide than in pure water. It would appear, therefore, that the theory of the common ion only holds when the solutions are so dilute that their dissociation is approximately complete, and where complex reactions are absent.

Another difficulty in the application of this theory to magmas is that little is definitely known as to the physical or chemical state of a fused salt. Lehmann has advanced a fusion theory which assumes two liquid states, regarded by him as physical isomers. Fusion is in his view a passage from the solid to a physically isomeric liquid modification. At high temperatures, far above the melting point, all the substance is in the liquid modification, but, on cooling, the solid modification begins to form, and remains dissolved in the liquid modification, until at the freezing point a supersaturated solution of the solid in the liquid form is present. He applies this theory to the explanation of the abnormal density of water near the freezing point. Between 0° C. and 4° C. water holds still some solid ice in solution, and only above 4° C. does it consist entirely of the liquid modification.[1] Tammann has recently discussed a similar theory.[2]

[1] *Lehmann*, Molekularphysik, i. 682; ii. 441; Zeit. f. Kryst., i. 104, 1877; Zeit. f. Phys. Chem., xxi. 17, 1896.

[2] *Tammann*, Zeit. f. Phys. Chem., xxi. 17, 1896.

With regard to the chemical state of fused salts here has been much divergence of opinion. It is known that fused salts follow Faraday's laws of electrolysis,[1] but there has been much speculation as to whether the molecules in a fused mass are in a combined state, or whether they exist as free oxides.

Some maintain, for example, that olivine does not exist as such in a liquid magma, but that the union of magnesia and silica only takes place in the act of crystallization. To this view there are many objections. As Harker has pointed out,[2] it is difficult to conceive the complete suspension of chemical affinities which the free oxide theory would involve. If, also, magmas consist of free oxides, the number of possible combinations of these would be large, whereas the actual number of rock-forming minerals is very limited. There are many minerals, such as wollastonite, monticellite, andalusite, cordierite, periclase, etc., which occur frequently as products of rock metamorphism, but are not known to occur as primary constituents of igneous rocks. This fact alone would be very difficult to explain on the free oxide theory.

On the other hand, it is very clear that the actual minerals occurring in the solid state in rocks were not in all cases present as such in solution in the magma. This applies more particularly to mix-crystals, as, for example, labradorite, which would probably be represented in the magma by molecules of albite and anorthite. In the same way, fayalite would be present in the magma as forsterite and iron olivine. In addition to this, chemical reactions are continually going on in the magma with corresponding interchange of acids and bases. It is possible, as Harker states, that some

[1] *Lorenz*, Zeit. f. Electrochem., vii. 277-287, 1900.
[2] *Harker*, Natural History of Igneous Rocks, p. 165; see also Science Progress, No. 6, p. 239, 1907.

of the minerals mentioned above as absent in igneous rocks may actually be present in the magma, but do not appear in the final stage owing to chemical reactions of this character.

On the whole, it seems probable that the only free oxides present in the magma would be confined to excess of silica, alumina, iron oxides, and water.

Influence of Complex Ions.—The influence of complex ions must also be considered. This may be illustrated by the solubility of calcium carbonate in natural waters. One of the fundamental facts of chemical geology is the greatly increased solubility of calcium carbonate in water containing carbon dioxide in solution. At first sight it might be thought that this is a direct contradiction of the law of the common ion described above, since both salt and solvent might be supposed to contain $\bar{C}O_3$ ions. In fact, however, if the calcium bicarbonate which is formed in solution in water containing carbonic acid were completely ionized, the reversible equation would be

$$CaCO_3 + H_2CO_3 \rightleftarrows \overset{+}{Ca} + 2\bar{H}CO_3.$$

For equilibrium by Ostwald's law we have, supposing the active mass of $CaCO_3$, which is present in excess, to be constant, concentration of Ca ions × concentration of $HCO_3$ ions = $k$ × concentration of $H_2CO_3$.

But by the above equation it is seen that the concentration of the $HCO_3$ ions should be double that of the Ca ions. Therefore, if $c'$ represent the latter, and $c''$ the concentration of the $H_2CO_3$, we have

$$c'.(c')^2 = kc''; \text{ that is, } (c')^3 = kc'', \text{ or } c' = k\sqrt[3]{c''}.$$

But as $c''$ is proportional to the partial pressure $p$ of the superincumbent carbon dioxide gas,

$$c' = k'\sqrt[3]{p} = k'p^{0.333}.$$

This result was investigated by Schloesing,[1] who found by actual experiment

$$c' = kp^{0.3786}.$$

The discrepancy was probably due to the fact that the ionization of the dissolved $Ca(HCO_3)_2$ was not complete.

Schloesing concludes that the proportion of calcium bicarbonate in solution depends, for any given temperature, upon the tension of the $CO_2$ present in the air. The smallest diminution in this tension destroys the equilibrium, and causes a precipitation of $CaCO_3$, with an escape of $CO_2$ until a balance is again reached.

Thus the influence upon the solubility of calcium carbonate of $CO_2$ is not opposed to the theory of the common ion, since an entirely different salt is formed, with a higher solubility product.

Velocity of Reaction.—In the case of many minerals formed in Nature by chemical precipitation from solution, the reacting masses are often exceedingly small. Becke[2] has described the formation of barytes from the warm springs of Teplitz, in which barium is present in such minute quantity that its presence is not recognizable by ordinary analytical methods, and yet crystals of barytes reaching 5 centimetres in diameter are formed by precipitation from the waters.

In such cases the influence of time is great. The velocity of reaction is, in fact, sometimes so slow that it is almost inappreciable. This velocity is influenced by other factors than the concentration of the ions. Temperature, pressure, the nature of the solvent, the presence of other substances, all exert a marked influence upon the rapidity of the reaction. In the case of heterogeneous reactions—viz., those in which

[1] Comptes Rendus, lxxiv. 1552, 1872; lxxv. 70, 1872.
[2] Tschermak. Min. u. Pet. Mitt., v. 82, 1883.

substances in different states are concerned, such as between a solid and a liquid, a very frequent occurrence in geology—both the extent and nature of the solid surface influence the velocity of reaction. This was proved by Boguski in experiments on the action of acids upon Carrara marble.[1] Spring, also, working with crystals of Iceland spar, found that the velocity of solution varied on the different crystal faces,[2] and Ostwald has given other illustrations of a similar nature.[3]

Hamberg[4] found that the velocity of solution of calcite in a 15 per cent. solution of hydrochloric acid was nearly four times as great on the face 2R as on the face R. The difference was smaller in more dilute solutions, owing possibly to the more complete ionization of the solvent.

Similarly, polymorphic forms have different solubilities. Anhydrite takes three or four times as long as gypsum to form a solution of given strength, supposing the solvent to be continually renewed, and calcite is not so readily dissolved as aragonite.

The importance of the time factor in geology, therefore, cannot be overestimated. The time necessary for chemical changes to take place varies enormously according to the circumstances of the case. Old rocks may remain apparently unaltered, where newer rocks are more or less completely transformed. For example the St. Peter sandstone of Wisconsin and the Cambrian sands of Russia are still almost in their original state while the tertiary rocks of the coast range of California and of the Alps are profoundly metamorphosed.[5] The influence of time on the attainment of equilibrium

[1] Berichte, ix. 1646, 1876. [2] Zeit. f. Phys. Chem., ii. 13, 1888
[3] Lehrbuch d. Allg. Chem., ii. 127, 128.
[4] Zeit. f. Kryst., xx. 398; see also *Becke*, Tschermak. Min. u. Pe Mitt., xi. 349.
[5] *Van Hise*, Treatise on Metamorphism, p. 43.

conditions is also well shown by certain phenomena connected with the cooling of rock magmas and slags. Vogt found that on quickly cooling a molten slag of a certain composition spinel crystals, containing a considerable proportion of lime, separated ; but by cooling more slowly spinel free from lime was obtained. Similarly, he obtained monticellite by rapid cooling, and forsterite or fayalite by slow cooling.[1] This latter fact possesses geological interest in view of the fact that natural olivines are remarkably free from lime, monticellite being only known at present as occurring in the zone of contact metamorphism. Pure lime olivine, $Ca_2SiO_4$, has only recently been formed artificially, and is not with certainty known to occur in Nature, pointing to the probability that calcium orthosilicate is a labile substance under such conditions, and only exists under circumstances of false equilibrium.

The above described differences between quickly and slowly cooled silicates illustrate Ostwald's law that in all transformations the stable form is not necessarily reached at once, but that intermediate labile forms may first appear.[2]

Time, therefore, is an indispensable factor in geological equilibrium, and its importance increases with the slowness of the velocity of reaction.

Catalysis.—This consideration leads naturally to the subject of catalysis. Catalyzers appear to act in the same way as enzymes by increasing or retarding the velocity of reaction. In the case of enzymes the reactions principally influenced are those in which the heat change is very small, and the equilibrium point, at which the reaction is reversible, lies approximately midway between the two extremes, as illustrated

[1] *Vogt*, Silikatschmelzlösungen, p. 95.
[2] *Ostwald*, Grundlinien der Anorg. Chem., p. 215, 1900.

above (see Fig. 42, p. 186). Catalyzers produce no displacement of the equilibrium, since they do no work appreciably, and hasten or retard both the direct and the reverse action. It is important to note that all true catalytic actions are distinguished by the fact that the catalyzer, itself present in a very small proportion, can influence large quantities of the reacting substances without appearing to enter into the reaction. This limitation of the term catalysis, however, is not often adopted by geologists. Doelter, for example, extends it to all cases of acceleration or retardation of reactions by the presence of an intermediate substance, without reference to the way in which the latter acts.[1]

The importance of catalytic processes in geological chemistry is undoubtedly great. Ostwald[2] has stated that "there is probably no kind of chemical reaction which cannot be influenced catalytically, and there is no substance, element, or compound which cannot act as a catalyzer." Amongst such processes familiar in geology may be placed the action of minute quantities of moisture, and the influence of solid substances in inducing crystallization in supersaturated solutions.

The extent to which catalysis enters into the phenomena of the crystallization of rock magmas is a much debated point. The term "agents minéralisateurs," first used by Elie de Beaumont, was restricted by St. Claire Deville to gases, which, while not entering into the composition of minerals, yet impart to them a tendency to crystallize.[3] The conception has since been extended by Michel Lévy and the French school to explain a large number of phenomena. In the opinion of Morozewicz, Lagorio, Vogt, and other

[1] Physikalisch-Chemische Mineralogie, p. 117, footnote.
[2] Zeit. f. Electrochem., vii. 995, 1905.
[3] Comptes Rendus, lii. 920, 1264, 1861.

authorities, the scientific limitations of the catalytic theory have been exceeded, since many of the so-called "agents minéralisateurs" do enter into the composition of the minerals which they are assumed to influence—as, for example, in the case of fluorine in certain micas, tourmaline, and topaz, boron in tourmaline, carbon dioxide in cancrinite, etc. It is evident that such actions are not strictly catalytic in character, and the unrestricted use of the expression "agents minéralisateurs" has destroyed its value as a geological term.

Morozewicz gives an example of what appears to be true catalytic action in the case of hydrofluoric acid. If this acid is passed over amorphous alumina, there is formed aluminium fluoride, $AlF_3$, thus:

$$Al_2O_3(\text{amorph}) + 6HF = 2AlF_3 + 3H_2O.$$

By the action of water this substance is decomposed with the formation of corundum, thus:

$$2AlF_3 + 3H_2O = Al_2O_3(\text{corundum}) + 6HF.$$

Thus a small quantity of hydrofluoric acid is capable of converting an indefinite quantity of amorphous alumina into corundum, and the reaction is typically catalytic in character.[1]

There are many chemical processes which would not be expected to be influenced by catalytic action. Of this kind we may take the case of the atomic disintegration of radio-active substances such as uranium. If any means were known whereby this process could be accelerated, the consequences would be of the utmost importance. But this is not to be expected upon theoretical grounds, because atomic disintegration is not only not reversible within the limits of present knowledge, but it is also accompanied by a considerable

[1] Tschermak. Min. u. Pet. Mitt., xviii. 1 *et seq.*, 1898-99; see also *Vogt*, Silikatschmelzlösungen, ii. 217.

heat effect, and, as stated above, is not, therefore, likely to be thus influenced.

It is not necessary to enter further upon the theoretical aspect of this question, or to enumerate the various views that have been advanced in explanation of catalytic phenomena.[1] The ionic theory of catalysis, held by many chemists, may, however, be illustrated by a familiar example—viz., the extraction of gold from ores by the cyanide process. The presence of free oxygen greatly assists the solution of gold in dilute potassium cyanide solution. Its action is explained thus: The cyanide solution contains hydrogen ions, which discharge on the surface of the gold. The gold thus becomes polarized—viz., covered with a film of hydrogen—and solution is retarded. The presence of oxygen effects depolarization, with the formation of hydrogen peroxide, thus enabling the gold to dissolve. The action can be repeated indefinitely, and is purely catalytic in character.[2]

No general theory of catalysis seems to explain satisfactorily all the various phenomena included under this head. It has been suggested that the function of a catalyzer may be to direct the chemical transformation along a certain path, in preference to another, whereby the velocity of reaction is either accelerated or retarded.[3] Many of the so-called mineralizers ("agents minéralisateurs") probably have no chemical effect at all, but act by promoting the velocity of crystallization by diminishing the viscosity.[4] In other cases their function is to lower the melting point of certain minerals, thus enabling them to separate within the temperature limit of their stability.

[1] *Mellor*, Chemical Statics and Dynamics, p. 245 *et seq.*, 1904.
[2] *Maclaurin*, Journ. Chem. Soc., lxiii. 724, 1893; lxvii. 199, 1895.
[3] *Mellor*, Chemical Statics and Dynamics, pp. 322-326, 1904.
[4] *Doelter*, Physikalisch-Chemische Mineralogie, p. 117.

In some such way can be explained the separation of quartz instead of tridymite from acid magmas.

Another action of mineralizers, which is purely chemical and must not be confused with catalytic reactions, is illustrated by the relative stability of reciprocal salt pairs, a principle which has been elaborated mainly by the work of Meyerhoffer.[1] As an example may be given the artificial formation of scheelite by the reaction of sodium tungstate and calcium chloride, the double decomposition being represented by the equation :

$$Na_2WO_4 + CaCl_2 = CaWO_4 + 2NaCl.$$

This reaction is more complete in the presence of NaCl, because this salt modifies the solubilities of the salts concerned, and favours the stability of the salt pair on the right-hand side of the equation. Similarly, the reversibility of the transformation of leucite into analcime, studied by Lemberg,[2] seems to depend upon the nature of the salt pair selected, and the relative stability of the resulting triads.[3] Such phenomena are determined by solubility rather than by catalysis as usually defined by chemists.

Influence of Pressure on Chemical Activity.— The influence of pressure upon the velocity of chemical reactions is somewhat uncertain. Van 't Hoff states that upon thermo-dynamical grounds chemical reactions of the first order are independent of pressure, second order reactions are proportional to pressure changes, and third order reactions are proportional to the square of the pressure.[4] In the case of first order reactions this has been proved in a few instances.

[1] *Meyerhoffer*, Zeit. f. Phys. Chem., xxxviii. 323, 1901.
[2] Zeit. d. Deut. Geol. Gesl., xxviii. 530, 612, 1876 : xxxix. 506, 1887.
[3] *Doelter*, Physikalisch-Chemische Mineralogie, p. 205.
[4] *Van 't Hoff*, Vorlesungen über Theoretische und Physikalische Chemie, i. 235.

Röntgen found that the inversion of cane-sugar proceeded more slowly under a pressure of 500 atmospheres than under 1 atmosphere.[1] Planck found that ionic dissociation increases with increase of pressure if dissociation leads to a reduction of volume.[2] Rothmund concluded that pressure can either accelerate or retard the velocity of reaction, according to the relation of the specific volumes of the active and inactive molecules.[3] The question has also been investigated by Bogojawlensky and Tammann, with interesting results.[4] These authors find that weakly dissociated solutions are more strongly influenced by pressure than strongly dissociated solutions. At a pressure of 5,000 atmospheres acetic acid becomes twice as active as at ordinary pressures. They conclude that at a pressure of 50,000 atmospheres all acids and bases would be equally active.

This conclusion is particularly interesting from the point of view of chemical geology, because it is the weakly ionized molecules, such as silicic acid, alumina, water, etc., which play so important a part in intratelluric chemical reactions. Arrhenius has drawn attention to the possibility of the increased chemical activity of water under such conditions, and the part this substance may play in the decomposition of silicates and the liberation of silicic acid.[5]

Struve and Müller have shown that carbon dioxide under pressure has a greater power of decomposing silicates than under ordinary circumstances.[6] This is owing to the increase in the number of active molecules, and is in accordance with the law of mass action. At the same time, the actual kinetic energy of

[1] Wied. Ann., xlv. 98, 1892.
[2] *Ibid.*, xxxii. 495, 1887.
[3] Zeit. f. Phys. Chem., xx. 168, 1896.
[4] *Ibid.*, xxiii. 13, 1897.
[5] *Arrhenius*, Zur Physik des Vulkanismus, Geol. Fören. Förh. Stockholm, pp. 395-419, 1900.
[6] Tschermak. Min. u. Pet. Mitt., vii. 47, 1877.

the molecules of a gas under pressure is reduced by the crowding of the molecules and their mutual interaction, as indicated in the law of Guldberg and Waage. For this reason the chemical activity of gases is not simply proportional to the pressure. It is probable that many chemical reactions which take place upon the surface of the earth either cease or are reversed at a greater depth, especially when considerable volume changes result. Thus, hydration below the surface may be partially or entirely checked by pressure, owing to the resistance to expansion. On the removal of pressure, hydration may take place so rapidly as to cause disintegration. This result has been noted by Merrill in the granitic rocks of Columbia,[1] and by Daly in the sedimentary rocks from certain railway cuttings in Brazil.[2] It also has been noted in the Foxdale granite in the Isle of Man.[3] These rocks are in a state of potential hydration, restrained by pressure and the want of room for expansion. The reversibility of chemical reaction under pressure is indicated in the action of carbonic acid upon silicates. At the surface of the earth carbonic acid decomposes silicates, but the frequent abundance of carbonic acid in deep-seated waters points to the silication of carbonates in plutonic regions, with liberation of carbonic acid gas, as suggested by Bischof.[4] If this reversibility did not exist, carbonic acid would tend to become fixed, and the amount present in the free state would diminish. This is not necessarily opposed to the observations of Struve and Müller referred to above, because the high temperature of plutonic regions may contribute to the reversibility. Bischof noticed that even at

[1] *Merrill*, Rocks, Rock-Weathering, and Soils, p. 188, 1897.
[2] *Daly*, Journ. Geol., iv. 529-540, 1896.
[3] *Lamplugh*, Geology of the Isle of Man, p. 509, 1903.
[4] Chemical and Physical Geology, i. 6, 237-241, 1854.

100° C. silicic acid, when present in excess, can partially decompose carbonates.

The same principle is also illustrated by Spring's experiment on the effect of a pressure of 6,000 atmospheres on the reaction :

$$BaCO_3 + Na_2SO_4 \rightleftharpoons BaSO_4 + Na_2CO_3.$$

Using molecular proportions of the above substances, this reaction was found to proceed in either direction, the direct change taking place to the extent of 80 per cent. and the reverse change to the extent of 20 per cent.[1] Under a sufficiently high pressure, therefore, sodium sulphate would not completely precipitate barium from solution.

We may here consider the general influence of pressure on solubility. In the case of salts dissolved in water, the volume change accompanying solution is in most cases small, and is usually negative, so that increase of pressure favours solubility. The influence of pressure, however, is not generally so great as that of temperature. This fact has been emphasized by Spezia, who showed that the solvent action of water upon quartz is far more dependent upon temperature than upon pressure.[2]

There is a marked relation between solubility and vapour pressure. At a given temperature the less stable phase is the more soluble, and has the higher vapour pressure, as has already been explained (see p. 81), and a reversal of solubilities can be brought about by pressure changes, as already described.

With regard to the influence of pressure on the fusion curve, this point has already been discussed (see *ante*, Section I.). It is probable that in intratelluric regions isothermal crystallization may take place under

[1] *Nernst*, Theoretical Chemistry, p. 390, 1895.
[2] Acad. reale della Scienza di Torino, 1895-96.

the influence of pressure alone. This conclusion follows from the shape of the fusion curve. The order of consolidation in this case would depend upon the relative value of $\frac{V_2 - V_1}{L}$ for different minerals (see p. 8). It is also possible that a separation may take place between the first formed crystals and the mother liquor, either by the gravitation of the former or by a squeezing out of the latter. Thus the resemblance of apophyses to their batholiths would depend upon the extent to which crystallization had taken place before the fissures were injected. Greisen might thus represent the mother liquor of a granite magma. There may thus arise a deep-seated magmatic differentiation of a nature akin to the crystallization differentiation so often observed in rocks which consolidated by slow cooling near the surface. Thus the pressure factor affords a means whereby these two processes of differentiation, which have generally been held to be so essentially different in character, may be reduced to one common cause—viz., the separation of the mother liquor from a partially crystallized magma. It would also explain the parallelism between the crystallization sequence and the differentiation sequence. It must be stated, however, that this view of differentiation is not accepted by Vogt, who maintains that magmatic differentiation is due to a separation of fluid phases.[1]

It is also noteworthy that pressure crystallization might cause a reversal of the normal order of consolidation. For since the direction of the fusion curve depends upon the value of the factor $\frac{V_2 - V_1}{L}$, it is probable that the value of this factor is different for

[1] *Vogt*, Über Anchimonomineralische und Anchieutektische Eruptivgesteine, p. 6, 1908.

different minerals. Consequently, the fusion curves under increasing pressures would cut one another, and the relative fusibilities would ultimately be reversed, as shown by the diagram (Fig. 43).

Lagorio,[1] also, has called attention to the influence of pressure changes in different parts of an ascending

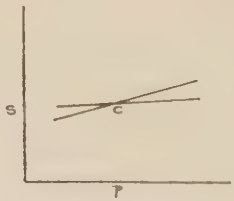



FIG. 43.—REVERSAL OF NORMAL ORDER OF CRYSTALLIZATION BY PRESSURE.

eruptive mass. Resorption might in such cases follow, owing to the lowering of the solubility curve under diminished pressure. Vogt illustrates this by the accompanying diagram (Fig. 44), in which the upper curve represents the relative solubility of two minerals under high pressure and the lower curve

FIG. 44.—INFLUENCE OF PRESSURE ON RESORPTION.

that for low pressure. The actual displacement of the equilibrium curve for a pressure variation of one atmosphere was calculated by Barus, and found to be 0·025° C.[2] This value is probably too large on account

[1] Tschermak, Min. u. Pet. Mitt., p. 510, 1887.
[2] Phil. Mag., Ser. 5, XXXV., 1893.

of too small a value being found for the latent heat by Barus.[1] Leaving the actual value of the difference out of the question, it is obvious from the diagram that the liquid phase region under the low-pressure conditions overlaps the solid phase region under the high-pressure conditions, and that crystals separating under the high pressure would tend to be remelted under the lower pressure. As the temperature continually falls, the amount of resorption that will take place will depend upon the time during which the temperature falls from a point on the higher curve to a point on the lower curve. It will also depend upon the relative solubility of the mineral in the magma, and upon its latent heat of fusion. This phenomenon, therefore, may be due—(1) to supersaturation, as shown on p. 152; (2) to change in the composition of the magma, as in the process of separation of mix-crystals; (3) to pressure changes, as described above. Resorption, therefore, is not always to be considered a result of pressure changes. The term "magmatic corrosion," also, often used to denote this phenomenon, is not strictly correct, because it implies a chemical action which may or may not accompany it.

Influence of Strain on Chemical Action.—Judd[2] has suggested the distinction between static and dynamic metamorphism. It is, therefore, of interest to consider the influence of strain on chemical reactions. Barus has shown that energy is potentialized[3] when metals are in a state of strain, and Hambuchen[4] has proved experimentally that when metals are in a state of strain they are more readily acted upon chemically than when free from strain. Van Hise adduces examples of the same principle in

[1] *Vogt*, Die Silikatschmelzlösungen, ii. 161.
[2] Geol. Mag., p. 243, 1889.
[3] Bull. U.S. Geol. Surv., No. 94, pp. 107, 108, 1892.
[4] Bull. Univ. Wisconsin, No. 42, p. 255, 1900.

geology.[1] Devitrification of unannealed glass is an adjustment of molecules releasing themselves from strain, and the development of secondary minerals in many schists is possibly connected with the same principle. Lepsius concluded that the minerals developed in crystalline schists have a smaller molecular volume than those from which they originated,[2] a theory which has been further developed by Becke.[3] Although this is what theory demands, there is a difficulty in calculating the molecular volumes of minerals owing to the uncertainty which exists as to the extent to which polymerization has taken place under the influence of pressure or other causes. Vogt attempted to determine the molecular weights of certain minerals by determining the molecular depression of the freezing point, using Van 't Hoff's formula. From these experiments he concludes that there is no polymerization in the case of minerals separating from slags, but that other minerals, such as hornblende, have a more complex molecule, and are probably polymerized.[4] Clarke, on the other hand, finds reasons for assuming extensive polymerization of the silicates.[5] It cannot be stated, therefore, with any certainty that pressure tends as a general rule to the formation of complex molecules, or that the so-called high-pressure minerals are polymerized.

Probably of greater importance is the increase of solubility of minerals under stress. Becker and Day[6] have recently investigated the growth of crystals under this condition, and find that the growth of

[1] Treatise on Metamorphism, p. 657 *et seq.*
[2] Zeit. d. Deut. Geol. Gesell., p. 530, 1893.
[3] Denkschriften d. Wiener Akad., lxxv. 28, 1903.
[4] Die Silikatschmelzlösungen, i. 41.
[5] Bull. U.S. Geol. Surv., No. 125, 1895.
[6] Proc. Wash. Acad. Sci., vii. 283-288, 1905.

crystals in the plane normal to the pressure is vastly greater than their development in the direction of the pressure. Stress, therefore, tends to induce crystalline orientation. The direction of elongation of crystals will in general follow the plane of least resistance.

In such cases solution would be expected to take place along the line of greatest strain, and deposition would follow along the normal plane.[1]

Schistose rocks, therefore, afford a further illustration of the general law of equilibrium, which states that when the equilibrium of a system is disturbed, the system tends to return to equilibrium by elimination of the disturbing element.[2] Molecular adjustments, however, may also be brought about by mechanical means, such as crushing or flow, without any marked chemical action.

[1] Amer. Journ. Sci., xxii. 224, 1906.
[2] *Bancroft*, The Phase Rule, p. 4, 1897.

# INDEX TO AUTHORS


Adams, F. D., 17, 78
Aimé, G., 77
Aitken, J., 56
Akerman, R., 5, 158
Alkemade, R. van, 159, 160
Allen, E. T., 2, 7, 22, 23, 32, 34, 82, 84, 103, 115, 163
Allport, S., 155
Amagat, E. H., 20
Armstrong, E., 84
Arrhenius, S., 30, 75, 132, 208

Bäckström, H., 132, 133
Bancroft, W. D., 103, 215
Barlow, W., 99, 173
Barrois, C., 52
Barrow, G., 106, 145
Barus, C., 9, 10, 23, 28, 29, 91, 96, 193, 212, 213
Battelli, A., 43
Bauer, E., 105, 128
Beaumont, E. de, 204
Becke, F., 64, 113, 114, 149, 163, 201, 214
Becker, G. F., 40, 49, 70, 78, 132
Beilby, G. T., 16, 43
Bemmelen, J. M. van, 87, 88, 90
Berthollet, L. C., 189
Bischof, G., 209
Bödlander, G., 73
Boeke, H. E., 107
Boeris, G., 106
Bogojawlensky, A., 208
Boguski, J. G., 202
Bois-Raymond, E. du, 70
Boudouard, O., 104
Bourgeois, L., 78
Brauns, R., 85, 97, 104, 109, 124
Brögger, W. C., 38, 44, 47, 48, 53, 134, 155, 172
Brun, A., 5
Buchanan, J. Y., 136
Bunsen, R., 54, 149

Callender, H. L., 43
Cameron, F. K., 66, 71, 93, 95, 196
Carveth, H. R., 166, 168, 182
Chaperon, G., 49, 50, 51
Chapuis, J., 89
Charpy, G., 141
Chrustschoff, K. v., 78, 112, 113
Clarke, F. W., 66, 93, 96, 99, 111, 214
Clement, J. K., 115
Coblentz, W. W., 81
Cohen, E., 2, 20
Cole, G. A. J., 52
Collomb, 50
Credner, H., 64, 109
Cusack, R., 5
Cushman, A. S., 67, 68
Curie, P., 61, 62, 64

Daly, R. A., 37, 38, 52, 209
Damien, B. C., 10
Daniell, 41
Darwin, C., 33
Daubrée, G. A., 17, 91, 188
d'Ans, J., 124
Davis, W. A., 87
Day, A., 2, 7, 22, 23, 32, 34, 104, 138, 143, 144, 163, 214
Debray, H., 76
De Lapparent, A., 51
Delesse, A., 96
Demerliac, R., 10
Deville, H. St. C., 40, 204
Doelter, C., 4, 9, 10, 20, 21, 22, 23, 26, 27, 29, 32, 44, 52, 73, 91, 104, 129, 148, 194, 204, 206, 207
Dorsey, N. E., 68
Duhem, P., 77
Durocher, J., 31, 51, 132

Emerson, B. K., 78, 79
Eotvos, R., 58
Erlenmeyer, E., 81

Evans, J. W., 91
Ewing, J. A., 17, 136

Fermor, L. L., 79
Ferro, A. A., 90
Findlay, A., 81, 131
Fock, A., 81
Foote, H. W., 107, 108
Fouqué, E., 28, 149, 174, 175
Foussereau, G., 21, 194
Freundlich, K., 71
Friedel, C., 89, 91

Geikie, Sir A., 20, 34, 55, 91
Geuther, A., 106
Gibbs, Willard 60, 162
Goodchild, J. G., 52
Gosselin, R., 141
Gouy, M., 49, 50, 51
Graham, T., 39
Greenly, E., 41
Groom, T., 113
Guthrie, F., 138, 139

Haidinger, W., 107
Hall, Sir J., 77
Hallock, W., 74
Hamberg, A., 202
Hamilton, J. F., 58
Harker, A., 27, 28, 31, 48, 49, 50, 54, 55, 91, 96, 135, 145, 150, 151, 153, 197, 199
Hautefeuille, P., 110
Hawes, G. W., 78
Hayes, C. W., 93
Heddle, M. F., 90, 113
Heim, A., 95
Helmholtz, H. v., 21, 66
Henry, W., 41
Heycock, C. T., 138, 181
Hise, C. R. van, 72, 73, 95, 96, 97, 107, 111, 112, 188, 202, 213
Hissink, D. S., 168, 182
Hoff, J. H. van 't, 13, 42, 71, 74, 83, 84, 93, 94, 105, 116, 117, 120, 121, 123, 124, 125, 126, 147, 185, 186, 187, 190, 207, 214
Holland, Sir T. H., 36, 78, 97
Holmquist, P. J., 170
Hoppe-Seyler, G., 87
Hudson, C. S., 130
Hulett, G. A., 10, 58, 62, 82, 84
Hutton, J., 77

Iddings, J. P., 20, 23, 29, 63, 193
Isaac, F., 60, 154

Johnston-Lavis, H. J., 52, 53
Joly, J., 5, 31, 58, 104
Jones, O. G., 21
Judd, J. W., 55, 72, 115, 182, 213
Jüptner, H. v., 132, 133, 155

Kahlenberg, L., 43, 66, 191
Kelvin, Lord, 96
King, F. H., 70
Klein, C., 107
Klobbie, E. A., 88
Kohler, E., 69
Kohlrausch, F., 92
König, 21
Königsberger, J., 105
Kramers, J. C. H., 45
Küster, F. W., 163

Lacroix, A., 52, 54, 183
Ladd, G. E., 65, 70
Lagorio, A., 33, 47, 146, 149, 170, 204, 212
Lamplugh, G. W., 209
Lane, A. C., 164
Lawson, A. C., 55
Le Chatelier, H., 1, 9, 76, 78, 86, 107
Lehfeldt, R., 45
Lehmann, O., 3, 13, 18, 50, 60, 64, 198
Leith, C. K., 97
Lemberg, J., 35, 91, 207
Lenarčič, J., 129
Lepsius, R., 214
Lincoln, A. F., 66
Linder, S. E., 66
Lœwinson-Lessing, F., 32, 44, 50, 51, 53, 92, 132, 133, 134
Lorentz, R., 45, 199
Lucion, M., 86
Ludvig, C., 46

Mack, E., 10
Maclaurin, R. C., 206
Mallard, E., 23, 107
Marr, J. E., 151
Maxwell, C., 19
Mellor, J. E., 190, 206
Mendeléef, E., 104
Merrill, G. P., 209
Meyerhoffer, W., 126, 151, 152, 153, 207
Michel-Lévy, A., 28, 52, 149, 204
Miers, H. A., 25, 31, 36, 60, 61, 111, 154, 155
Moissan, H., 74, 75, 110

Monckman, J., 69
Morozewicz, J., 33, 104, 149, 204, 205
Muck, F., 89
Müller, R., 208, 209
Müller, W. J., 105

Nernst, W., 36, 133, 196, 210
Neville, F. H., 138, 181
Newth, G. S., 132
Newton, Sir I., 19
Nicolson, J. T., 17

Ochsenius, C., 127
Oetling, C. F., 20
Osann, A., 74
Ostwald, W., 10, 13, 25, 59, 61, 62, 72, 92, 100, 109, 193, 200, 202, 203, 204

Pattinson, H. L,, 142
Payen, A., 49
Perman, E. P., 35, 191
Pictet, R., 13
Picton, H., 66
Piotrowski, 21
Pirrson, L. V., 31, 91
Planck, M., 10, 208
Pope, W. J., 81, 99, 173
Popow, S. P., 50
Pöschl, V., 164, 166
Pošepný, F., 87
Poynting, J. H., 10, 41, 57, 67, 86
Pratt, J. H., 135
Prior, G. T., 172

Quensel, P. D., 105
Quincke, G., 57, 66

Ramsay, Sir W., 83
Ramsden, W., 68
Rayleigh, Lord, 67
Reicher, L. T., 100, 103
Retgers, J. W., 30, 64, 85, 172
Reuter, M., 196
Richards, T. W., 95
Roberts-Austen, Sir W. C., 9, 41
Rodger, J. W., 19, 20
Röntgen, W. C., 208
Roozeboom, H. W. B., 10, 14, 100, 101, 102, 160, 161, 163, 165, 167, 168
Rose, G., 87, 107, 108, 190
Rosenbusch, H., 31, 132, 150
Rosenhain, W., 136
Rothmund, V., 130, 208
Rücker, Sir A. W., 9
Rudler, F. W., 109
Ruff, O., 88
Rutley, F., 63

Schaum, K., 109
Schlœsing, T., 65, 201
Schönbeck, W., 109
Schreinemakers, F. A. H., 177-181
Schulze, H., 65
Scrope, G. P., 50
Seidell, A., 95
Shepherd, E. S., 104, 138, 143, 144
Skeats, E. W., 82
Skey, W., 69
Smeeth, W. F., 113
Smith, A., 129
Sollas, W. J., 52
Sommerfeldt, E., 90
Sorby, H. C., 72
Soret, C., 46
Spezia, G., 210
Spring, W., 10, 41, 65, 93, 94, 202, 210
Stead, J. E., 141
Stefanini, A., 43
Stokes, H. N., 111
Streng, A., 112
Struve, F. A. A., 208, 209

Tait, P. G., 70
Tammann, G., 9, 10, 11, 12, 24, 35, 90, 100, 101, 107, 198, 208
Teall, J. J. H., 34, 47, 63, 79, 112, 113, 146, 150, 155
Thaddéef, C., 171
Thomson, Sir J. J., 41, 57, 67, 69, 71
Thorpe, T. E., 19, 20
Tommasi, D., 88
Törnebohm, A. E., 78
Traube, H., 43
Treadwell, F. P., 196
Trechmann, C. O., 111
Trener, G. B., 42
Tresca, H., 10
Troost, L., 40
Tschermak, G., 111, 126, 175
Tutton, A. E., 98, 99

Usiglio, B., 83, 123, 124, 125

Vater, H., 64, 87
Vernadsky, W., 106
Vogelsang, H., 63, 133

Vogt, J. H. L., 6, 23, 27, 28, 31, 32, 33, 44, 55, 61, 99, 103, 111, 133, 146, 150, 153, 158, 165, 166, 170, 172, 175, 181, 182, 196, 197, 203, 204, 205, 211, 212, 213, 214
Vučnik, M., 26
Vukits, B., 26

Walker, T. L., 78
Waltershausen, S. v., 51
Washington, H. S., 113
Way, J. T., 70
Weed, W. H., 69
Weinschenk, E., 111
Wenzel, C. F., 190
Weyprecht, K., 136
Whetham, W. D., 69, 92
White, W. P., 102
Wijs, J. J. A., 92
Wright, C. R. A., 130
Wright, F. E., 115
Wulff, G., 30

Zambonini, F., 90
Zirkel, F., 31

# INDEX TO SUBJECTS


Absorption spectra of hydrates, 81
Adsorption, 70, 71, 72, 73
Agents Minéralisateurs, 32, 204, 205
Alloys, freezing curve of, 141, 142, 143
Alumina, influence of, 33
Amphibole, stability of, 111, 112, 113, 114
Analcime in igneous rocks, 91, 92
Andalusite, 106
Anhydrite, formation of, 83, 84-87
Anorthite, fusion curve of, 7
Aragonite, stability of, 106, 107, 108, 109
Assimilation hypothesis, 51, 52
,, of magmas, 54

Binary systems, fusion curves of, 136, 137, 138, 139
Borax, crystallization of, 35
Border segregation in magmas, 47, 48, 55

Calcite, primary, in igneous rocks, 78, 79
,, stability of, 79, 106, 108, 109
Calcium carbonate, solubility of, 200, 201
Capillarity, 68, 69
Capillary attraction, 64
,, constant, 61
Carnallite, formation of, 119, 120
Carnot-Clausius principle, 184, 185
Catalysis, 203-206
Cementation of rocks, 72, 73
Chlorite, hydration of, 90
Colloidal suspension, 65, 66
Colloids, 66
Common ion, 195-198
Complex ions, 200
Composite dykes, 55
Convection currents, 49
Cooling curves, 6
Co-solutes, influence of, 63, 64, 85
Critical point, 2
Crystalline surfusion, 23
Crystallization, spontaneous, 36
,, tendency, 28
,, velocity, 25, 29
Cyanite, 106

Devitrification, 35
Diamond, 110
Diffusion, cause of, 42, 43
,, of gases, 39
,, Graham's law, 39
,, of liquids, 42
,, of magmas, 44
,, Nernst's formula, 36
,, of solids, 41
,, and viscosity, 36, 49
Dissociation of calcium hydrate, 75, 76, 77
,, of hydrates, 82
,, of magnesium carbonate, 79

Electric conductivity of silicates, 24, 45
Enantiotropic substances, 99, 100
Energy isobars, 34
Equilibrium adjustments in solids, 41
Eutectic composition, 146, 147
,, structure, 155
,, ternary, 155, 156

False equilibrium, 13, 34
Faraday's laws of electrolysis, 45
Fick's law of diffusion, 43
Flow of solids, 16, 17, 18
Fluxes, influence of, 28, 30, 32
Fusibility and solubility, 149, 150
Fusion curve, 8
,, ,, of binary systems, 137

Fusion curve, influence of pressure on, 9, 10, 11
„ „ influence of viscosity on, 22
Fusion point, definition of, 8
„ „ of minerals, 4, 5
„ „ lowering of, 138, 147
„ „ of isomorphous mixtures, 163
„ „ under stress, 13, 14, 15
Fusion, theory of, 198, 199

Garnet, fusion of, 23
Glass in Beinn Hiant rocks, 34
„ in Eskdale dyke, 34
„ in Tynemouth dyke, 34
Glasses, composition of, 33
„ formation of, 34
Glassy structures, 32, 34
Globulites, 63, 133
Gold, crystallization of, 36
Gravitation in magmas, 50
„ and viscosity, 31, 37
Gravity, influence of, on diffusion, 49
Guldberg and Waage, law of, 209
Gypsum, dehydration of, 84
„ vapour pressure of, 82, 83

Hybrid rocks, 54
Hydrates, classification of, 83
„ constitution of, 80
Hydration in nature, 95, 96, 97
Hydrolysis, 92, 93
Hypertectic point, 155

Inoculation, 25
Intrusion of magmas, 20, 38
Ionic viscosity, 24
Ionization of silicates, 193
Iron hydrates, 87
Isotonic solutions, 44, 46

Labile state, 60, 63
Latent heat of fusion, 8
Le Chatelier, principle of, 1
Lime-silica series, 143, 144
Liquid crystals, 3, 10

Magmas, viscosity of, 20, 27
Magmatic differentiation, 46, 47, 48, 49, 50, 51-55, 132-135, 145
Magnesia pyroxenes, 115
Marble, flow of, 17
Mass action, 189, 190
Matter, states of, 2
Meldometer, 5, 58
Melting-point, definition of, 3
Metastable state, 59, 63
Mineralizers, 30, 32, 203-206
Mix-crystals, conditions of formation of, 170, 171
„ „ definition of, 116
„ „ melting point of, 7, 159, 163
„ „ in ternary systems, 173
„ „ Type I., 161-163
„ „ Type II., 164
„ „ Type III., 164
„ „ Type IV., 166
„ „ Type V., 168
Molecular depression of freezing point, 147
Monotropic substances, 99, 100
Morphotropy, 172

Non-consolute liquids, 51, 129
Normal order of consolidation, 150, 151
„ „ reversal of, 150, 151, 154, 212

Oil process of mineral separation, 59
Oscillatory equilibrium in magmas, 153, 154
Osmotic pressure, 42, 46, 47, 48
Osmotic theory, 53

Pattinson's process, 142
Polymerism, 98, 214
Polymorphous substances, melting point of, 7, 99-105
Porphyritic crystals, 29, 31
Potential, definition of, 158
„ thermo-dynamic, 158, 159
Pressure and dissociation, 76, 77, 93
„ influence of, on chemical action, 207 213
„ influence of, on crystallization, 211, 212
„ influence of, on the fusion curve, 8, 9, 10, 11, 12
„ influence of, on polymerization, 98, 214
„ influence of, on resorption, 212, 213
„ uniform, and stress, 13
„ and viscosity, 20
Pseudo-Monotropy, 100

Pseudo-Wollastonite, 103
Pyrites, stability of, 110, 111
Pyroxene, stability of, 111-114

Quartz, deformation of, 18
„ stability of, 104, 105

Recurrent series, 177
Resorption, causes of, 213
Reversal of normal order of consolidation, 150-154, 212
Reversible reactions, 185-187, 190
Rock weathering, principles of, 193

"Schlieren," 55
Sequence of eruption, 145
Sillimanite, stability of, 106
Sodium chloride, solubility of, 117-119
Solid diffusion, 40, 41
„ solution, definition of, 116
„ state, changes in, 181-183
Solubility curves, 117
„ and fusibility, 149, 150
„ product, 191
Soret's hypothesis, 46
Space-model applied to igneous magmas, 127, 128
„ „ of Stassfurt salts, 125
Stassfurt salts, 83, 94, 117, 119-127
Strain, influence of, on chemical action, 213
Stress, influence of, on melting point, 13-15
Sublimation curve, 75
Sulphur, stability of, 100-102
Superfusion, 23
Supersolubility curve, 60
Surface tension and chemical action, 67-70
„ „ and crystal growth, 59, 60, 63
„ „ definition of, 56
„ „ influence of temperature on, 58
Surface tension of liquids, 57
„ „ and solubility, 62, 202
„ „ and supersaturation, 56

Tensimeter, 81
Ternary systems, mix-crystals in, 173-176
Thermo-dynamic potential, 158-160
Thermo-dynamic potential, graphic represention of, 159
Thermo-dynamic surfaces, 161
Titanium oxides, stability of, 110
Transition point of hydrates, 81, 82
Tridymite, stability of, 104-105

Vapour pressure, influence of co-solutes on, 85, 86
„ „ of solids, 74, 75
„ „ and solubility, 81
Velocity of chemical action, 201, 202
Viscosity, definition of, 19
„ influence of, on the cooling curve, 7
„ influence of pressure on, 20
„ and ionization, 24, 194
„ of magmas, 27, 37
„ measurement of, 21
„ and order of crystallization, 151-153
„ and rock structure, 28
„ and superfusion, 24
„ variability of, 31, 32
„ of water, 20
Volume change in dehydration, 94

Water of crystallization, 80, 81
„ influence of, in chemical reactions, 35, 190, 191
Wollastonite, stability of, 103

Zenoliths, suspension of, 37
Zeolites, constitution of, 89

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721